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AIR POLLUTION: CONTROL TECHNIQUES FOR SULFUR OXIDE AIR POLLUTANTS

NATO Committee on the Challenges of Modern Society

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FOR
SULFUR OXIDE
AIR POLLUTANTS

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PREPARED FOR
THE COMMITTEE ON THE CHALLENGES
OF MODERN SOCIETY

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October, 1973

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FOREWORD

This document is a compilation of information on methods for the control of sulfur oxide that was assembled by the Expert Panel for Air Pollution Control Technology, The Committee on the Challenges of Modern Society, NATO, for distribution to the member countries.

The Chairman of the Expert Panel wishes to acknowledge the efforts of scientists from the pilot countries, scientists from observer countries, and the many other persons who assisted in the preparation of this document and the four companion volumes: Control Techniques for Carbon Monoxide Emissions from Stationary Sources, Control Techniques for Particulate Air Pollutants, Control Techniques for Hydrocarbon and Organic Solvent Emissions from Stationary Sources and Control Techniques for Nitrogen Oxide Emissions from Stationary Sources.

Thanks are due the Environmental Protection Agency of the United States for permission to use their document, Control Techniques for Sulfur Oxide Air Pollutants which was published in 1969, as a basis for this effort. Representatives from this agency deserve special recognition.

Major contributions were made by a team of scientists from the Federal Republic of Germany under the direction of Dr. Dieter Hartmann. These contributions were invaluable to the success of the effort.

Recognition should also be given to the team from the Research Triangle Institute, Research Triangle Park, North Carolina, USA, for their efforts in literature searches, writing, and editorial work.

Lastly, acknowledgment should be given to those secretaries and other support personnel who have made the panel effort possible.

John K. Burchard, Ph.D.
Panel Chairman

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SUMMARY

Sulfur oxides (SO_2 and SO_3) found in ambient air originate from both stationary and mobile sources. The term SO_x is used herein to indicate the sulfur oxides singly or as mixtures. Of the 30.94 Gkg of sulfur oxides produced by industrial, commercial, and domestic sources in 1970, 20.2 Gkg were emitted from coal combustion, 3.8 Gkg from fuel oil combustion, 7.6 Gkg from industrial processes, and the balance primarily from waste disposal and transportation. Data from the Federal German Republic are referenced as BRD (Bundes Republik Deutschland).

SOURCES OF SULFUR OXIDES

Stationary Combustion Sources

About 95 percent of the total energy in the United States is supplied by fossil fuels. In 1969, coal supplied about 21 percent of the energy; petroleum, about 40 percent; and natural gas, about 36 percent.

Sulfur oxide emissions from these sources were about 24 Gkg in 1970, or about 78 percent of the total SO_x emissions. Electrical utilities accounted for about 17.6 Gkg, or 73 percent of the total originating from stationary sources.

Industrial Sources

The primary industrial sources of sulfur oxides emissions are nonferrous smelters, petroleum refineries, sulfuric acid plants, iron and steel plants, pulp and paper mills, and waste disposal. Other industrial sources that emit relatively small quantities include glass manufacture, corn starch production, sugar refining, sulfur fusion processes, sulfur dioxide production, silicon carbide production, titanium dioxide production, and organic sulfonation.

Estimated emissions of sulfur oxides from industrial sources are given in Table 1.

CONTROL METHODS

Methods for controlling sulfur oxides emissions include energy source substitution, combustion process modification, fuel desulfurization and waste gas cleaning.

In energy source substitution, sulfur oxide emission reduction is directly proportional to reduction of sulfur in fuel. Availability, applicability, and cost of the fuels with lower sulfur content are critical factors in applying this method.

Combustion process modifications that offer promise of reducing sulfur oxides emissions are high and low pressure fluidized bed combustion, combined cycle operation, and fluid bed gasification. Until these processes are developed further, the most practical modification is the use of higher pressure steam for power generation.

Coal cleaning techniques, which include crushing and flotation, are already being used to a limited extent. The sulfur reduction accomplished depends on the pyrite content of the coal. Few coals can be upgraded to a product containing 1 percent sulfur or less. Cleaning and flotation are not considered effective sulfur reduction techniques in the BRD.

Catalytic treating with hydrogen removes sulfur from oil. Blending low-sulfur-content distillate oils with residual oil also lowers sulfur

Table 1. SUMMARY OF SULFUR OXIDES EMISSIONS FROM MAJOR INDUSTRIAL PROCESSES, 1970

Process	Emissions, 1000 Kilograms
Pulp and paper	69 900
Calcium carbide	1 800
Sulfuric acid	546 100
Coking	430 000
Smelters	4 091 400
Refineries	325 700
Total	5 464 900

content. For a typical east coast imported residual fuel oil, a 60-percent sulfur reduction can be achieved, and greater reductions are possible.

Waste gas cleaning has received considerable interest in the past several years. Commercialized processes in the United States include limestone-based processes (limestone addition to the scrubber, lime addition to the scrubber, and limestone injection to the boiler), sodium solution scrubbing both with evaporative regeneration and with no by-product, and direct conversion to acid. Other developmental activities in the United States include char sorption, sodium solution scrubbing with electrolytic regeneration, and adsorption on reactive solids. Outside the United States, operational systems include ammonia scrubbing, lime slurry scrubbing, sodium solution scrubbing, absorption in sulfuric acid, catalytic copper oxide, activated carbon, and Lurgi processes. The cost of waste desulfurization is estimated to be 1 to 4 mils/kwhr depending on conditions.

EMISSION FACTORS

Emission factors may be used to estimate emissions from sources for which accurate stack test results are unavailable. Process emission factors are presented in Chapter 6.

1. INTRODUCTION

Sulfur oxides in the atmosphere are known to have many adverse effects upon health and welfare, and reduction of emissions of these pollutants is of prime importance to any effective air pollution abatement program. This document has been prepared to summarize current information on sulfur oxide air pollutants--sources and methods of control.

Sulfur oxides originate from a variety of sources, and the emissions vary widely in physical and chemical characteristics. The many agricultural, commercial, domestic, industrial, and municipal sources of sulfur oxide pollutants are described individually in this document. The nature and quantities of the emissions from the various processes are discussed, and methods of control that have been successfully applied are listed.

The control techniques described herein represent a broad spectrum of information from many engineering and other technical fields. The devices, methods, and principles have been developed and used over many years, and much experience has been gained in their application. They are the techniques generally applicable to the broad range of sulfur oxide emission control problems.

1.1 THE SULFUR OXIDES

An oxide of sulfur is any chemical combination of sulfur and oxygen This report, however, deals with only two such oxides, sulfur dioxide (SO_2) and sulfur trioxide (SO_3), which are the most common sulfur oxide pollutants. Sulfur dioxide is an invisible, nonflammable, acidic gas. It oxidizes to SO_3 in the atmosphere at varying rates, depending on temperature and the presence of other substances. Sulfur trioxide is a highly hydroscopic gas, which combines with water in the atmosphere to form sulfuric acid mist (H_2SO_4) or with other materials in the atmosphere to form sulfate compounds.

1.2 MAJOR SOURCES

Sulfur oxides, primarily SO_2, are generated during the combustion of any sulfur-bearing fuel and also by many industrial processes that use sulfur-bearing raw materials. In 1970, approximately 32.5 Gkg of sulfur oxides were emitted in the United States.[1,2] As shown in Figure 1-1, 24.0 Gkg, or about 74 percent of the national total, was produced by fuel combustion in stationary sources. Industrial processes added an additional 7.3 Gkg while the remainder (1.2 Gkg) was emitted by burning coal refuse banks, agricultural burning, combustion of fuels for transportation, and disposal of solid wastes. Obviously, the distribution of sulfur oxide emissions by source in any given locality may differ markedly from those of Figure 1-1.

In the absence of controls, it has been estimated that SO_2 emissions will increase with time as shown in Figure 1-2. This increase is due primarily to the projected increase in fuel consumption by utility companies; however, it is expected that the demand for fossil fuels will level off around 1990 as conventional fuel-burning power plants are replaced by nuclear stations.

Table 1-1 shows a breakdown of SO_2 emissions during 1970 from the various stationary fuel combustion sources. Fuel combustion is the largest source of SO_2 emissions because of the relatively high sulfur content of some bituminous coals and fuel oils and because of the large

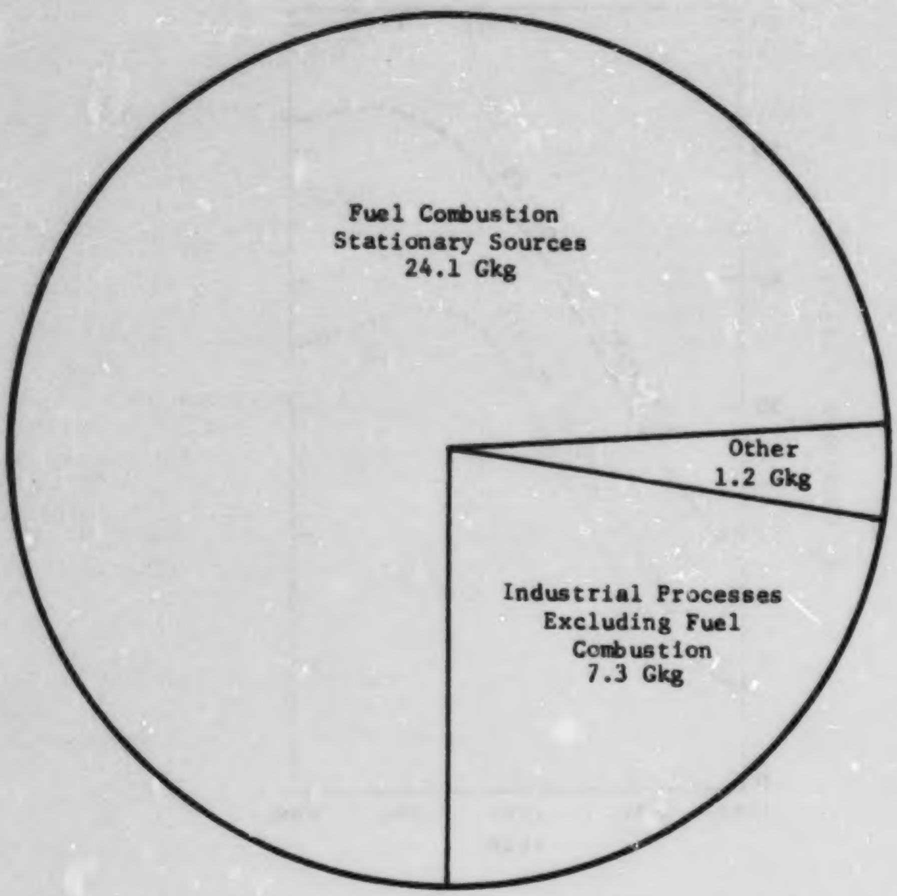


Figure 1-1. Nationwide sources of sulfur dioxide emissions, 1970.

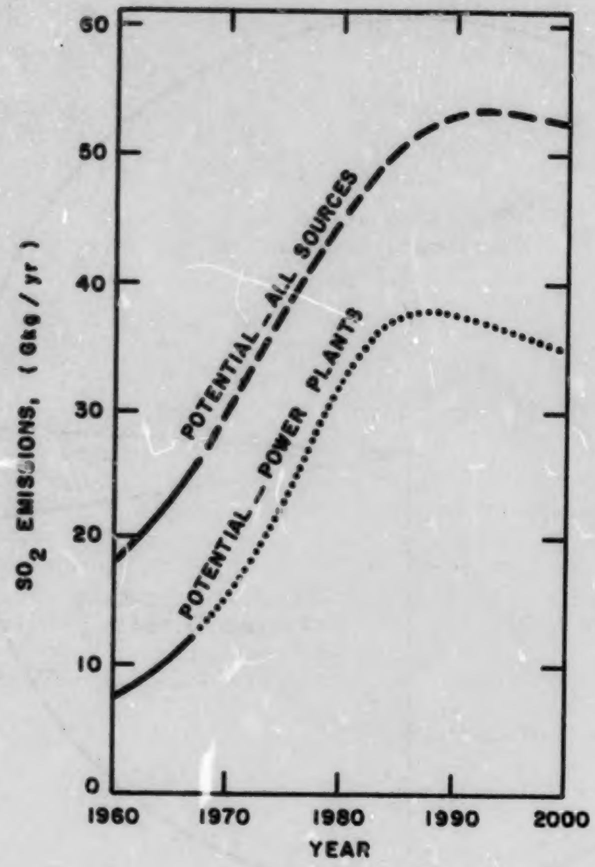


Figure 1-2. Estimated SO_2 emissions.[3]

Table 1-1. SO_2 EMISSION ESTIMATES FOR FUEL COMBUSTION IN STATIONARY SOURCES, 1970[1]

Sources	SO_2 emissions (Gkg)
Utility coal	16.06
Utility oil	1.519
Other coal (industrial, commercial, residential)	4.082
Other oil	2.314
Natural gas	0.005
Wood	0.029
Total	24.010

quantities of these fuels consumed. Bituminous coal and residual fuel oil usually contain from 1 to 3 percent sulfur by weight. Data on BRD fuels show 0.8 to 1.3 percent sulfur for bituminous coal and 0.3 to 1.8 percent for residual fuel oil. For every kg of sulfur burned, about 2 kg of SO_2 and 0.03 kg of SO_3 are formed.

Sulfur dioxide emissions during 1970 from industrial process sources are shown in Table 1-2. Smelting of metallic ores and oil refinery operations are the major industrial process sources of SO_2 emissions. However, it is anticipated that increased efficiencies of sulfur recovery facilities associated with these operations and the application of stack gas desulfurization techniques will tend to reduce (or at least prevent increases in) future emissions from these sources.

Table 1-2. SO_2 EMISSION ESTIMATES FOR INDUSTRIAL PROCESS SOURCES, 1970,[1,2]

Sources	SO_2 emissions (Gkg)
Smelters	4.1
Refineries[2]	2.1
Sulfuric acid plants	0.55
Coke processing	0.43
Pulp and paper	0.07
Calcium carbide	0.002
Total	7.252

1.3 SOURCE TESTING FOR SULFUR OXIDES

When it is necessary to quantify the amount of sulfur oxides emitted from a particular source, it is often necessary to perform stack gas sampling.

Many source tests are conducted to determine whether a particular source is complying with emission regulations. Testing for compliance is especially applicable to processes subject to new source performance standards. Source tests are also performed to determine the true efficiency of emission control devices, especially where the theoretical source emission (calculated with emission factors or by material balance) approximates the code limitation. Where alterations in a process design may be needed to correct pollution, source test results are often used as a basis for suggesting changes which will be most effective.

The U.S. Environmental Protection Agency published a detailed procedure for measuring sulfur dioxide from combustion sources.[4] The following methods are also commonly used in source testing and may be required by some state or local regulations:

1. Shell Development Company Method[5,6]
2. Los Angeles County Air Pollution Control District Method[7]
3. Total sulfur oxides, API Method 774-54[8]
4. Reich Test for sulfur dioxide[9]
5. Bureau of Mines Method No. 4618 for sulfur dioxide and sulfur trioxide[10]
6. Determination of sulfuric acid mist, sulfur dioxide, and sulfur trioxide.[11]
7. VDI Richtlinien chemical-analycital methods for measurement of SO_2 concentration in stack gases[12]
8. Automatic infrared-absorption measurement.[13]

A variety of continuous SO_2 stack gas monitoring instruments is also available. These instruments have not been used extensively to date. These instruments employ flame photometry, nondispersive infrared, correlation spectrometry, and ultraviolet light absorption as measuring techniques.

1.4 DESULFURIZATION PROCESSES

A comprehensive report on flue-gas desulfurization has recently (June 1973) been prepared under the sponsorship of the Federal Minister for Research and Technology of the Federal German Republic (BRD). This is an interim report under the title: Zwischenbericht "A" zur Systemanalyse Entschwefelungsverfahren. The coordinating editor is Dr. B. Forck. Text description, flow sheets, and process costs are given in this document.

REFERENCES FOR CHAPTER 1

1. OAP Data File of Nationwide Emissions, 1970. EPA, July 1972.
2. Laster, L. L. "Air Pollution Aspects of the Petroleum Refining Industry."
3. Rohrman, F. A., and Ludwig, J. H. "SO_2 Pollution: The Next 30 Years," Power, May 1967, pp. 82-83.
4. Federal Register, Vol 36, No. 247, Part II, December 23, 1971.
5. "Determination of Sulfur Dioxide and Sulfur Trioxide in Stack Gases." Shell Development Company, Emeryville Analytical Dept., California, Method Series 4S16/59a, 1959.
6. "Atmospheric Emissions from Sulfuric Acid Manufacturing Processes." U.S. Public Health Service, National Center for Air Pollution Control, Washington, D.C. PHS Publication 999-AP-13, 1965, p. 127.
7. Devorkin, H., Ghass, R. L., Fudurich, A. P., and Kanter, C. V. "Air Pollution Source Test Manual." Los Angeles County Air Pollution Control District, Los Angeles, California.
8. "Manual for Analytical Control of Liquids and Gaseous Effluents from Petroleum Processing Plants." American Petroleum Institute, Refiners' Committee on Waste Disposal, New York, Revised, June 30, 1950.
9. "Sulfur Dioxide Gas Test (Reich Test) for Sulfuric Acid Plants Either Utilizing or Not Utilizing Air Quench." Monsanto Chemical Co., Engineering Sales Dept., St. Louis, Missouri.
10. Berk, A. A., and Burdick, L. R. "A Method of Testing for SO_2 and SO_3 in Flue Gases." U.S. Dept. of Interior, Bureau of Mines, R.I. 4618, January 1950, 9 pp.
11. "Gas Analysis of Sulfuric Acid Plants." Chemical Construction Corp., Technical Methods, Research and Development Laboratory, New York, August 1961.
12. VDI Richtlinien Nr. 2462, Blatt, 1, 2, and 3.
13. URAS, Hartmann and Braum A. G., Frankfurt/M.

2. SULFUR OXIDE SOURCES AND THEIR EMISSION

Major sources of sulfur oxides are combustion and certain industrial processes. In this chapter, descriptions of the processes most likely to generate sulfur oxide emissions and estimates of the quantities of SO_x emitted by the various sources are given. In Chapter 6, emission factors are tabulated.

Data from the Federal German Republic will be referenced as "BRD" (Bundes Republik Deutschland).

2.1 COMBUSTION PROCESSES

Fuel combustion is an exothermal process in which carbon and hydrogen in fuel are oxidized to carbon dioxide and water vapor. Other gases liberated in much smaller quantities during combustion include unburned hydrocarbons, carbon monoxide, oxides of nitrogen, and sulfur oxides. Formation of sulfur oxides is totally dependent on fuel sulfur content whereas hydrocarbon, carbon monoxide, and nitrogen oxides emissions are more closely related to combustion efficiency or some characteristic of the combustion process.

In general, efficient combustion is dependent on three basic parameters: time, temperature, and turbulence. Adequate time is required to complete the chemical reactions; the temperature must be sufficient to insure fuel decomposition and ignition (but limited where possible to minimize fixation of nitrogen oxides); and finally, proper turbulence is necessary for adequate mixing of fuel and oxygen in order to minimize emissions of unburned hydrocarbons and carbon monoxide.

2.1.1 Solid Fuels

Coal is the solid fuel of prime industrial importance; coke is of secondary importance; and materials such as wood, bagasse, lignite, and solid wastes are also sometimes burned for their fuel value. The advent of automatic equipment to replace hand-firing methods has greatly reduced particulate and visible emissions from solid-fueled furnaces. However, sulfur oxide emissions continue to be a problem when burning coke and bituminous coal because of their high sulfur content. The sulfur content of coal varies widely, even for the same type--e.g., bituminous mined in the same geographical region. Table 3-1 gives the distribution in sulfur content for coal types from various regions. Available techniques for desulfurizing these fuels are discussed in Section 3.3.1. SO_2 emissions from these and other combustion sources can be reduced to some extent by various stack gas cleaning methods as discussed in Section 3.4.

The most common types of fuel burning equipment used with coal (and coke) are summarized in Table 2-1. Pulverized coal-fired boilers in electric power generating stations consume more coal than any other single source in the United States.[1] In these plants, the coal is pulverized to a median size of about 50 μm, mixed with air, and blown into the furnace. As with liquid fuels, combustion is rapid and can be closely controlled. In comparison with stokers, pulverized-fuel furnaces characteristically emit small quantities of unburned hydrocarbon gases but emit 50 to 80 percent of the ash in the coal as fly ash and thus require high-efficiency dust collectors.[1] Almost all of the sulfur in pulverized coal appears as SO_2 or SO_3 in the flue gases. Combustion of lignite releases from 7 to 100 percent of its sulfur as SO_2 depending upon how much of it is combined with the ash.

Approximately 471 Gkg of bituminous coal and lignite and 7.3 Gkg of anthracite were consumed in the United States in 1970 (excluding consumption by railroads, ships, and vessels).[2] Electric power utilities and industries

Table 2-1. - COMMON USES OF VARIOUS FUEL-BURNING EQUIPMENT IN THE UNITED STATES

Equipment	Common use
Coal-fired:	
Hand-stoked	Residential, institutional, and commercial warm-air and boiler applications at capacities up to 5.3 GJ/hr input. (Used primarily in coal-producing areas.)
Single-retort underfeed stokers	Residential, institutional, and commercial warm-air and boiler applications at capacities up to 42.2 GJ/hr input.
Multiple-retort underfeed stokers Spreader stokers Traveling grate stokers Chain grate stokers Vibrating grate stokers	Water tube and fire tube boiler applications for institutional, commercial, and industrial heating at capacities in range of 5.3 to 212 GJ/hr input.
Oil-fired:	
High-pressure gun-type burners	Residential warm-air furnace or boiler applications at capacities up to 11.4 dm^3/hr distillate oil.
Low-pressure air-atomizing burners	Water tube and fire tube boiler applications for institutional, commercial, and industrial process heating with distillate or residual oil.
Rotary cup burners Steam atomizing burners High-pressure air-atomizing burners Sonic nozzles	Water tube and fire tube boiler applications for institutional, commercial, and industrial heating and power generation with residual oil.
Gas-fired:	
Premixing or atmospheric burners	Residential warm-air furnace or boiler applications and low-temperature industrial applications.
Nozzle mixing or power driven	Water tube and fire tube boiler applications for institutional, commercial, industrial, and power generation applications. (May be combination type to permit fuel oil firing when gas supply is interrupted.)

are the largest consumers of coal. Heating value of solid fuels consumed in the BRD in 1970 were the following: bituminous coal, 2 460 x 10^{15} J;[3,4] lignite, 900 x 10^{15} J; anthracite, 94 x 10^{15} J.[3,4] On the basis of specific emission of 0.697 kg x 10^{-9} SO_2/J, the total SO_2 emissions for 1970 in the BRD was 2 Gkg.[5]

Total emissions from coal combustion amounted to 20.2 Gkg for 1970.[2]

2.1.2 Liquid Fuels

Fuel oils in commercial and industrial use range from light distillate oils to heavy residual fractions and consequently vary widely in composition as well as in physical properties. Since liquid fuels must be vaporized before combustion, there are considerable differences among burners which must, of course, be tailored to fit characteristics of the fuel being burned. Fuel vaporization can be accomplished either within the burner, as exemplified by the high-pressure air atomizer depicted in Fig. 2-1, or outside of the burner, as is the case with the rotary cup burner (shown in Fig. 2-2) which sprays fuel droplets into the combustion zone. In general, most oil burners in use at the present time fall into one of the five major categories listed in Table 2-1. The selection of a particular burner is largely dependent on fuel viscosity and volatility.

It can be assumed that all of the sulfur in liquid fuels is converted to SO_2 (and SO_3) during combustion. Consequently, sulfur oxide emissions from liquid-fueled combustion sources vary as widely as does the sulfur content of these fuels. Sulfur concentrations may range from as little as 0.04 percent or less for light distillate oils up to 6 percent or more for residual oils. Oil desulfurization and stack gas cleaning techniques are discussed in Sections 3.3.2 and 3.4.

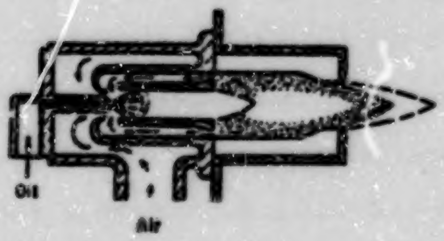


Fig. 2-1. The high-velocity burner produces combustion similar to hydroxylation because of the high heat release.[6]

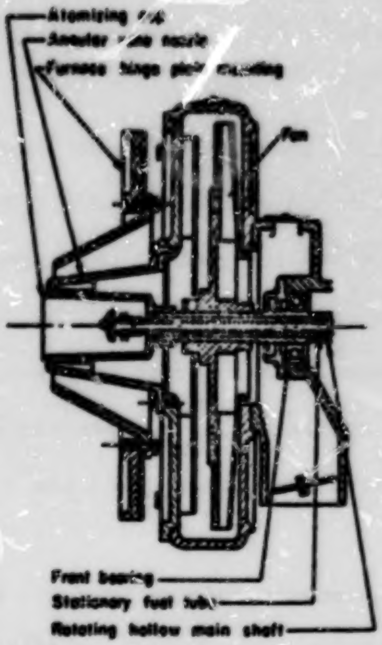

Atomizing cup
Annular air nozzle
Furnace hinge plate mounting
Fan
Front bearing
Stationary fuel tube
Rotating hollow main shaft

Fig. 2-2. The rotary-cup burner uses centrifugal force to spray oil from the atomizing cup.[6]

Approximately 100 hm^3 of distillate fuel oil and 114.6 hm^3 of residual fuel oil were consumed in stationary fuel combustion sources in 1970. Nearly 55 percent of the total fuel oil is consumed for space heating purposes in residential, commercial, institutional, and light industrial sources. Sulfur oxide emissions based on emission factors presented amounted to 3.8 Gkg for 1970 in the United States and 1.2 Gkg in the BRD. Data on fuel oils in the BRD are given in Table 2-2.

2.1.3 Gaseous Fuels

Gaseous fuels also vary considerably in composition and characteristics. For example, natural gases are primarily methane, while manufactured and coke oven gases are about one-half hydrogen and one-third methane; producer and blast furnace gases are of much lower heating value since they consist largely of nitrogen with the combustible portion being carbon monoxide and some hydrogen.[1] Composition of gaseous fuels determined in the BRD is given in Table 2-3.

Due to the low viscosity of gaseous fuels, gas burners are considerably simpler than those used with liquid and solid fuels. Most gas burners mix only a portion of the air required for combustion (primary air) with the fuel prior to ignition. Secondary air is drafted into the combustion chamber at essentially atmospheric pressure. In contrast to these atmospheric or premixing burners, power driven or nozzle mixing burners use blown air for intense mixing within the nozzle. These two burner types are compared in Figs. 2-3 and 2-4.[9]

In general, gas-fired equipment produces less air pollution than solid- or liquid-fueled burners, although poor burning conditions can temporarily result in small emissions of CO, organic gases, and vapors. Particulate

Table 2-2. - CONSUMPTION OF LIQUID FUELS IN THE BRD IN STATIONARY FUEL COMBUSTION SOURCES (1971)[7]

	Gkg	
Production	Gkg	
Distillate oil (D)	39[a]	
Residual oil (R)	32	
Consumption	D	R
Refineries	-	4
Industrial processes	7	22
Industrial power generation		3
Domestic	36	
Public power generation	3	2

[a] Without import

Table 2-3. - COMPOSITION OF GASEOUS FUELS IN THE BRD[8]

Gaseous fuels	Composition (Volume percent)				
	CO	CH_4	H_2	N_2	S mg/m^3
Natural gas	0	81	0	14.6	2-(150)
Coke oven gas		23	53	12	100-(250)
Fluid gas (LPG)					2-(120)
Sewer gas					100-20
Top gas (blast furnace)	30	0-3	0.5-4	60	

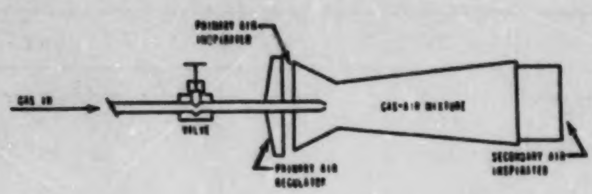

PRIMARY AIR INSPIRATED
GAS IN
VALVE
GAS-AIR MIXTURE
PRIMARY AIR REGULATOR
SECONDARY AIR INSPIRATED

Fig. 2-3. Typical atmospheric gas burner.[9]

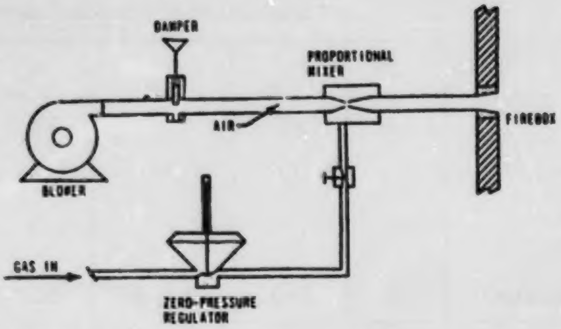

DAMPER
PROPORTIONAL MIXER
AIR
FIREBOX
BLOWER
GAS IN
ZERO-PRESSURE REGULATOR

Fig. 2-4. A multiple-port burner (nonprimary aerated) installed in a vapor incinerator.[9]

emissions are not produced unless a drastic restriction in air flow causes soot formation or unless there are residual solids present in the fuel.

Sulfur impurities in gaseous fuels occur primarily as hydrogen sulfide, although carbon disulfide contributes as much as 80 percent of the organic sulfur present in manufactured fuel gases.[6] Other sulfur compounds which may be present in small amounts are the thiophenes, carbon oxysulfide, mercaptans, thioesters, and organic sulfides. Essentially all of the sulfur compounds in fuel gas are converted to SO_2 or SO_3 during combustion.[1] Techniques for scrubbing or desulfurizing fuel gases are discussed in Section 3.3.3.

United States natural gas consumption exceeded 624 km^3 in 1970.[2] Electric power utilities consumed about 18 percent, gas pipelines and transmission about 14 percent, with residential, commercial, institutional, military, and industrial sources accounting for the remainder. Emissions in this category were only 5.5 Mkg in 1970.[2] In the BRD, gas consumption was 15.7 km^3 in 1970, 25 percent of which was used by electric power utilities.

2.2 INDUSTRIAL PROCESSES

The primary industrial processes that emit sulfur oxides are nonferrous smelters, petroleum refineries, sulfuric acid plants, iron and steel plants, pulp and paper mills, and waste disposal processes. Of lesser importance to the overall picture are minor sources--i.e., glass manufacture, corn starch production, sugar manufacture, sulfur fusion processes, liquid sulfur dioxide production, silicon carbide production, titanium dioxide production, and organic sulfonation.

2.2.1 Nonferrous Primary Smelters

Sulfur oxides emissions from nonferrous smelters are predominantly sulfur dioxide with varying proportions of other oxides such as sulfur trioxide. Emissions are normally discussed in terms of sulfur dioxide.

Copper, zinc, and lead usually occur as sulfides in mixed ores normally separated and concentrated at the mines by gravity separation, preferential wetting, or flotation. The resulting fractions, rich in metallic sulfides, are shipped to the smelters or refineries, which also usually separate gold, silver, cadmium, and molybdenum during the processing. Sulfur dioxide production is inherent in the smelting process.

In 1970, nonferrous smelters emitted about 11 percent of the total estimated sulfur oxide emissions in the United States.[2] Domestic production for each metal and sulfur oxide emissions are shown in Table 2-4.

In the BRD, SO_2 emissions from nonferrous primary smelters are reduced by the production of sulfuric acid. Roasting gases from the single copper smelter in the BRD and from lead and zinc smelters are desulfurized by double-contact acid plants processing feed gases containing 6 percent or more SO_2. Total acid production from these sources in 1970 was 770 Mkg.

2.2.1.1 Copper Smelters--Copper ore, or calcopyrite, normally contains less than 1 percent copper. Prior to smelting, the ore is concentrated to 15 to 32 percent copper by processes which are not sources of sulfur oxide emissions. Smelting extracts the copper from the concentrate and involves the use of roasters, reverberatory furnaces, and converters (Fig. 2-5). These are sources of sulfur oxides emissions, as shown in Table 2-5.

Roasting is practiced in about half of the U.S. smelters and is accomplished in multiple-hearth and fluid-bed roasters. Sulfur oxides

Table 2-4. - NONFERROUS SMELTER PRODUCTION AND SULFUR OXIDES EMISSIONS IN THE UNITED STATES, 1970[2,10]

(Mkg)

Metal	Concentrate	Metal production	SO_2 recovered	SO_2 emitted
Copper	7 610	1 500	710	2 585
Zinc	1 450	801	848	582
Lead	961	605	85	239
			1 643	3 404

Table 2-5. - SELECTED COPPER SMELTER DATA

Smelter source	Feed capacity 1 000 kg/day	Offgas data			After cooling and dust cleaning		
		Nm^3/s	Temp. K	SO_2, percent	Nm^3/s	Offgas temp., K	Offgas SO_2, % by vol.
Multiple-hearth roaster	135- 720	NA	920	5-10	NA	590	5-10
Fluid-bed roaster	635-1 360	NA	920	12-14	NA	590	12-14
Reverberatory furnace	360-1 000	21-28	1 590	0.5-2.5	28-40	480-530	0.25-2
Cylindrical converter	122	6-9.5	1 500	14-21	19-38	590	1.5-7
Hoboken converter	91	6-8.5	1 480	14-21	19-17	590	7-10

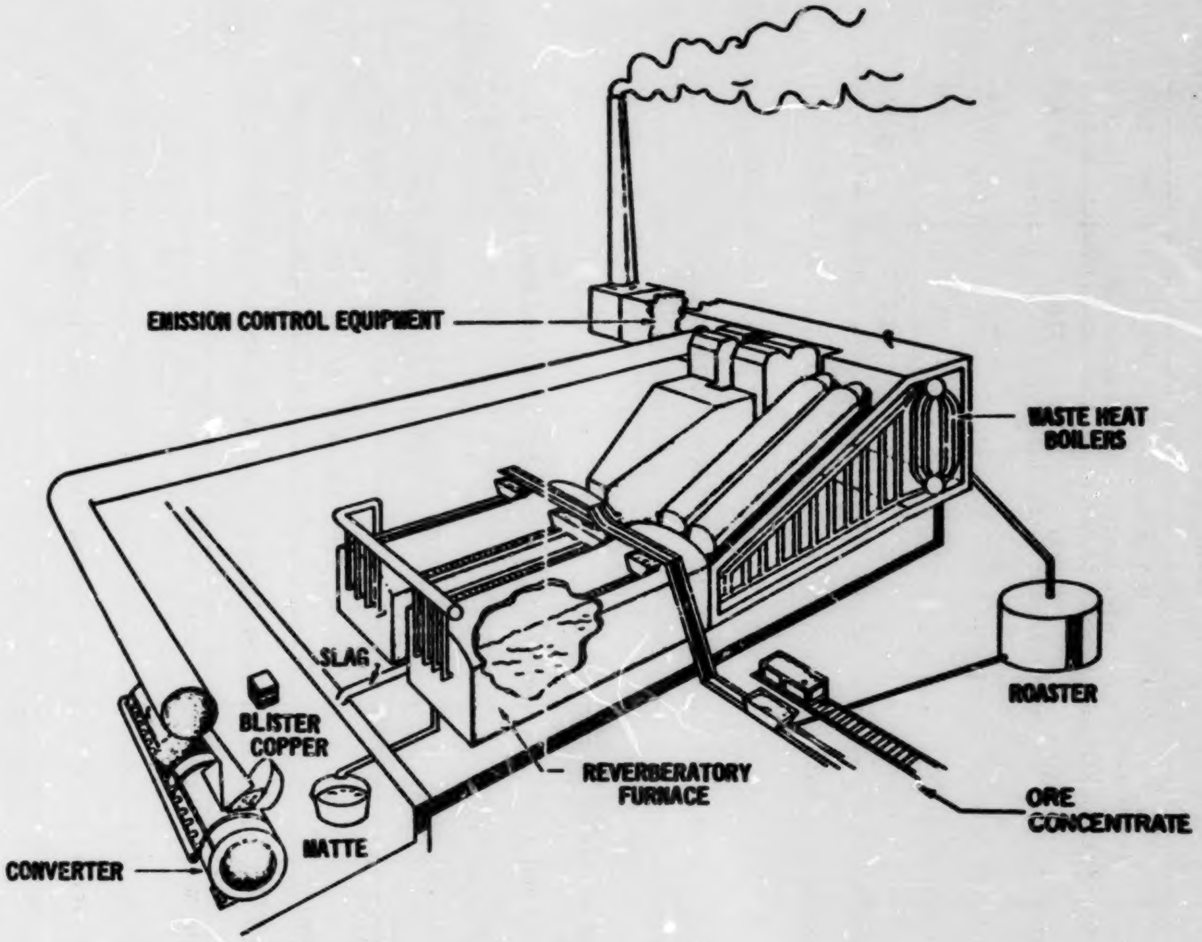

EMISSION CONTROL EQUIPMENT
WASTE HEAT BOILERS
ROASTER
ORE CONCENTRATE
REVERBERATORY FURNACE
SLAG
BLISTER COPPER
MATTE
CONVERTER

Fig. 2-5. Copper smelter.

concentration in the wet offgases from multiple-hearth roasters is usually 5 to 10 percent because of dilution with air; from fluid-bed roasters, the wet offgases contain 12 to 14 percent sulfur oxides. Both types of roasters produce relatively rich offgases amenable to sulfuric acid manufacture after cooling and dust removal. Roaster gases have also been used to enrich converter gases to provide more stable operations of the acid plant.[2,11]

Roasted or unroasted (green feed) material, along with liquid converter slag, is melted in a reverberatory furnace. Almost all of these furnaces in the United States are fired with natural gas, but fuel oil or pulverized coal can be used. Matte, which collects in the lower area of the furnace, contains 25 to 50 percent copper, 22 to 29 percent sulfur, and 30 to 35 percent iron.[12] Slag, the remainder of the molten mass, contains most of the impurities and is drawn off the top and discarded. The matte is periodically tapped from the bottom and charged to the converter.

When green feed is used as the charge to the reverberatory furnace, 20 to 45 percent of the sulfur in the feed is oxidized and removed with the offgases. Since substantial quantities of combustion air are required by reverberatory furnaces, the wet offgases contain about 1.5 to 3.0 percent sulfur dioxide.[13] If roasted feed is charged, concentrations are usually in the range of 0.25 to 1.0 percent.[13]

Molten matter from the reverberatory furnace is oxidized with air in converters to remove sulfur and iron; frequently, two converters are used for each reverberatory furnace. Converter gases are normally cooled by dilution with 1 to 4 volumes of air, which normally infiltrate at the hood covering the converter. Water cooling assisted by waste heat boilers may permit the use of close-fitting converter hoods. With conventional practice, the sulfur oxides concentration varies from 1 to 7 percent by volume at different stages of the converter cycle. When close-fitting hoods are used, the combined offgases from multiple converters are usually 4 to 6 percent.[10,13,14]

Over the past 25 years, several alternative smelting methods have been developed around the world in response to local raw materials availabilities, energy and labor costs, and byproduct markets. These methods include flash smelting, electric furnace smelting, continuous smelting, direct converter smelting, oxygen enrichment of air for blowing converters, and the Hoboken syphon converter.[15] All of these modified process techniques can, under carefully controlled conditions, yield gas streams containing from 10 to 25 percent sulfur oxides.

2.2.1 2 Zinc Smelters--Zinc occurs in the United States mainly as sulfide ores; the most common is sphalerite (ZnS). Ores which contain large amounts of lead sulfide and small amounts of iron and copper sulfides are concentrated by differential slurry flotation prior to smelting to increase the zinc content. These concentrates contain 52 to 60 percent zinc, 28 to 33 percent sulfur, and residual lead, iron, cadmium, and copper. There are presently seven zinc smelters in the United States (down from 14 smelters in 1968) with a capacity of 818 Mkg per year.[16] Six of these plants recover sulfuric acid from the roaster exit stream using single absorption systems.

In the smelting process, the concentrates are first roasted to convert the sulfides to oxides. If the zinc metal is to be extracted by reduction with carbonaceous fuel, it is first sintered to provide a hard, porous material and to volatilize impurities. If it is to be reduced electrolytically, it is dissolved directly in electrolyte. Several types of equipment and processes are used in domestic zinc smelters to accomplish the roasting and extraction steps.

The two sources of sulfur oxide emissions in zinc smelters are the roasters and, to a lesser extent, the sintering machines. Electrolytic reduction is not a significant source of sulfur oxide emissions. At pyrometallurgical smelters, from 90 to 99 percent of the sulfur combined as sulfide is oxidized by roasting. At electrolytic smelters, more than 99 percent of the sulfur combined as sulfide is oxidized in the roaster. Roasting is accomplished in several different types of furnaces, including reverberatory (Ropp), multiple-hearth (Herreshoff), fluidized bed, suspension or flash, fluidized column, and sintering furnaces. The capacities and sulfur oxide concentrations in the offgases differ somewhat (Table 2-6). The newer types--suspension and fluidized bed--have larger capacities and yield offgases rich enough for use as feed to a sulfuric acid plant (9 to 13 percent, decreased to 6 to 8 percent after dilution). A few of the older types of roasters are still in service; their offgases contain less than 1.5 percent SO_2.

The normal sintering operation uses a feed of calcined material (from the roaster), recycled ground sinter, recovered dust (in some plants), carbonaceous fuel, and possibly some raw concentrates. Between 30 and 80 percent of the total machine feed is usually recycled discharged sinter. The sintered product is a coarsely crushed material that is used for zinc extraction.

Waste gases from sintering contain variable concentrations of SO_2 ranging from 0.1 to 2.4 percent, depending on the quality of sinter desired,

Table 2-6. - EMISSIONS FROM ZINC-ROASTING PROCESSES

Type of roaster	Feed capacity, 1 000 kg/day	Dust in offgas, percent of feed	After cooling and dust cleaning		
			Offgas SO_2, % by vol.	Offgas temp., K	Nm^3/s
Ropp reverberatory	36-45	5	0.7-1.0	665-755	9.5-16.5
Multiple hearth	45-109	5-15	2.0-3.5	530-561	4.7- 7.1
Fluidized bed	127-218	50-80	6.0-9.0	530-390	5.2- 8.5
Suspension	109-318	50	6.0-8.0	530-590	8.0-11.8
Robson (combined sintering)	218-550	5-10	1.7-7.0	395-480	19.0-22.8

the residual sulfur in the calcined ore, and the raw sulfide in the feed.[10] The gases can be recirculated to the feed if raw concentrates are the major feed. In this case, sulfur dioxide concentrations of 6.0 to 6.5 percent may be obtained.[12]

2.2.1.3 Lead Smelters--Primary lead is derived from the sulfide mineral galena (PbS). The ore concentrate received at the smelter contains 55 to 70 percent lead by weight, 13 to 18.5 percent sulfur, and lesser amounts of zinc, iron, and copper, and other trace metals.[12]

Of the six lead smelters currently operating in the United States, three produce sulfuric acid from the smelter offgases. All of these acid plants are of the single-contact design and all operate only on a high concentration (3.5 percent or more SO_2) portion of the gas stream.

All primary lead smelters in this country use the same three processing steps--sintering of concentrates to convert the lead sulfide to the oxide, reduction of the sinter in a blast furnace, and refining in a dross reverberatory furnace and lead refining kettles. Many lead smelters have auxiliary associated operations, roasters for cadmium recovery, slag-fuming furnaces for zinc recovery, and deleading kilns.

Usually about 85 percent of the total sulfur in smelter feed is released during sintering; 14 percent enters the slag and other solid byproducts; and the remaining 1 percent is released in the blast furnace and dross furnace offgases.[12]

The sintering machine roasts the lead sulfides to form lead and sulfur oxides and produces a strong, porous mass suitable for blast furnace feed. Older sintering machines are of the downdraft type, in which the air is drawn through the charge by regulated windboxes below the continuous conveyors. Unrestricted infiltration of air dilutes the sulfur oxides concentration in the offgases to 1 to 3 percent.[10] Newer, larger sintering machines are of the updraft type, with windboxes located above the conveyors; these machines produce a much smaller volume of gas with concentrations ranging from 4 to 6 percent sulfur oxides from the feed-end windbox and around 0.5 percent from the discharge-end windbox.

The sinter is charged along with coke into the blast furnace, where free carbon and carbon monoxide at high temperatures reduce lead compounds to impure metallic lead. Sulfur dioxide concentrations in the furnace flue gas are 0.01 to 0.25 percent after dilution; dilution is necessary to reduce the temperature prior to dust collection and to burn the carbon monoxide.

The dross furnace separates lead from the matte and speiss (metallic arsenides). Emissions are low, since a surface dross layer that forms in the furnace inhibits oxidation of sulfur. The sulfur oxides in these offgases usually average less than 0.05 percent.[12] The lead-refining kettles generate less sulfur dioxide than do dross furnaces.

Emission data are limited for the other operations at lead smelters. Slag fuming furnaces emit about 0.02 percent; even lower emission levels are reported for cadmium roasters and deleading kilns.[12]

Several pilot studies of smelting operations are in progress. One domestic lead producer has been testing a converter in which the concentrates are smelted by air blowing; the offgases contained from 13 to 14 percent sulfur oxides.[11] A flash smelting process for lead concentrates has been tested on a pilot plant scale in Finland, where offgases contained 10 to 12 percent sulfur dioxides. In Sweden, a process for direct smelting of rich lead sulfide concentrates in an electric furnace has been placed in commercial operation; the offgases from the electric furnace contain about 6.0 percent sulfur oxides.

2.2.1.4 Control Methods--The technology to control emissions of sulfur oxides from copper, lead, and zinc smelters is based on the following techniques:

1. conversion of SO_2 in the offgases to SO_3 for the production of sulfuric acid,
2. reduction of SO_2 in the offgases to elemental sulfur,
3. reaction of SO_2 in the offgases to yield various sulfur compounds that can be discarded, reprocessed, or sold for use directly as obtained in other industries.

In addition, various process alternatives can be used to make smelting operations more amenable to emission control by the above techniques. Details of the offgas treatments listed above, along with cost estimates for emission control methods applicable to the primary industries, are given in Section 4.

2.2.2 Petroleum Refineries

Petroleum refining is the conversion of crude oil into usable products. In January 1972 there were 247 petroleum refineries in the United States with a combined crude oil capacity of 2.1 hm^3 per day.[17] Individual refinery capacities range from 160 m^3 to about 72 000 m^3.

Since the average sulfur content is 0.75 percent (ranging from 0.2 to 3.7 percent)[18] for domestic crude and 1.8 percent for imported crude,[19] refinery operations involve processing large quantities of sulfur. During 1970 estimated refinery sulfur oxide emissions amounted to 2.83 Gkg, or about 6.5 percent of the total SO_x emissions in the United States.[2,18]

In the BRD there are 35 refineries with a combined crude oil capacity of 126 Gkg per year. SO_2 emissions from these operations amounted to 135 Mkg in 1970, which accounts for 4 percent of total emissions of SO_2 from all sources in the BRD.[7]

Desulfurization procedures have long been an integral part of petroleum refining and have significantly reduced the sulfur content of gasoline and other distillate products. Environmental considerations have prompted further recent progress toward developing desulfurization techniques for heavy fuels as well as toward reducing sulfur oxide emissions from the various refinery processes.

Refineries differ depending on the degree of processing, the crude oil capacity, and the properties of the crude. The sulfur content of various crude oil feedstocks varies widely with the place of origin. This sulfur appears in various forms--as sulfides, mercaptans, polysulfides, and thiophenes. Since a single refinery may process as many as 50 different crudes in a calendar year, the emission control scheme must be able to handle a wide range of sulfur extraction rates.

Figure 2-6 shows the major processing operations for a typical modern refinery.[18] These operations can be grouped into four procedures--separation, conversion, treating, and blending. Separation, an essential operation common to all refineries, is accomplished by distillation; conversion, by cracking and reforming; treating, by numerous methods including the various desulfurization techniques; and blending, by combining stocks to form the finished petroleum products.

Sulfur oxide emissions in refineries originate from combustion, distillation, cracking, catalyst regeneration, reforming, polymerization and alkylation, and from several other miscellaneous sources.

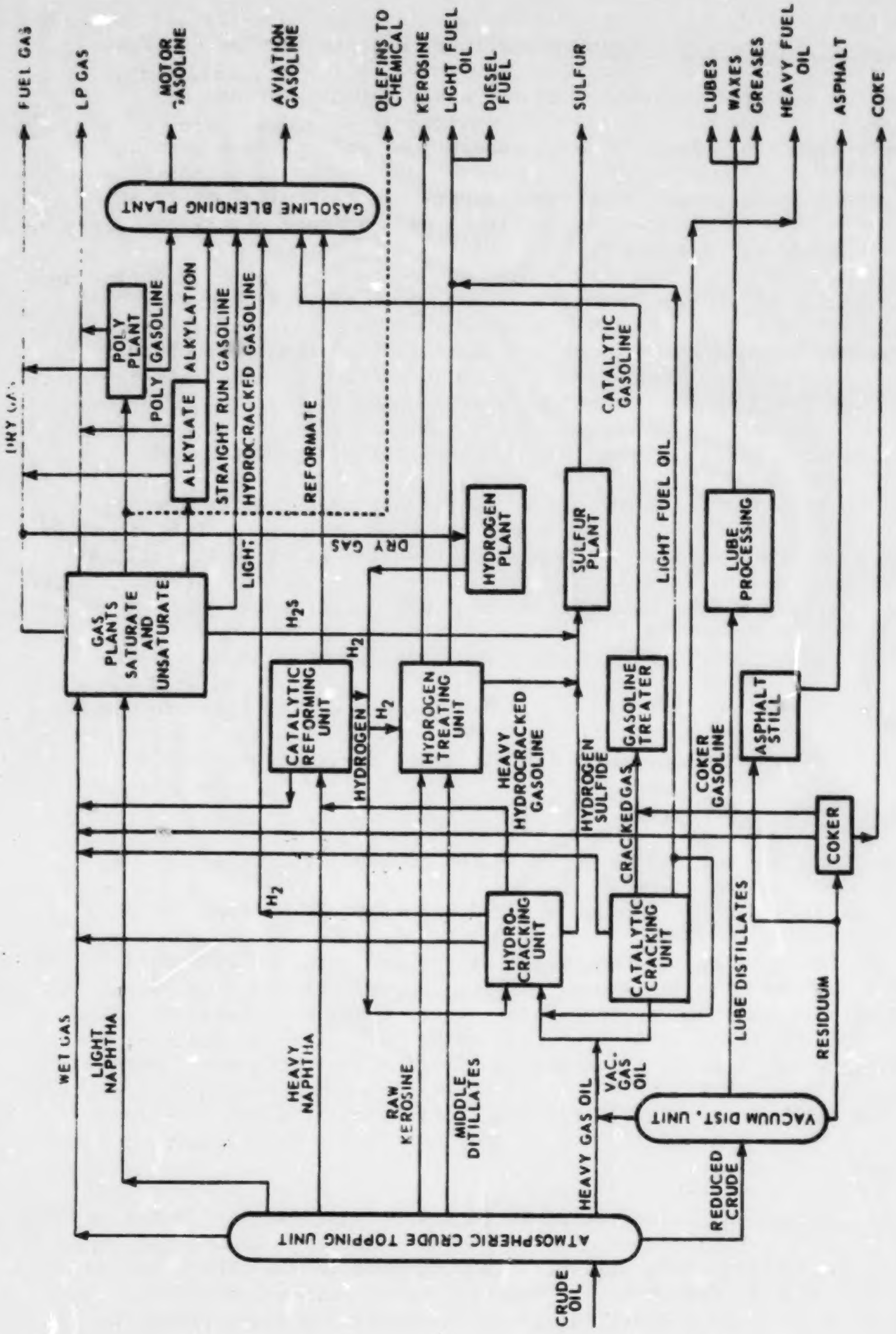

CRUDE OIL
ATMOSPHERIC CRUDE TOPPING UNIT
WET GAS
LIGHT NAPHTHA
HEAVY NAPHTHA
RAW KEROSINE
MIDDLE DISTILLATES
HEAVY GAS OIL
REDUCED CRUDE
VACUUM DIST. UNIT
VAC. GAS OIL
LUBE DISTILLATES
RESIDUUM
HYDRO-CRACKING UNIT
CATALYTIC CRACKING UNIT
H_2
CRACKED GAS
HYDROGEN SULFIDE
HEAVY HYDROCRACKED GASOLINE
HYDROGEN
CATALYTIC REFORMING UNIT
HYDROGEN TREATING UNIT
H_2
H_2
GAS PLANTS SATURATE AND UNSATURATE
H_2S
LIGHT
DRY GAS
HYDROGEN PLANT
SULFUR PLANT
GASOLINE TREATER
COKER GASOLINE
ASPHALT STILL
COKER
LUBE PROCESSING
LIGHT FUEL OIL
CATALYTIC GASOLINE
REFORMATE
HYDROCRACKED GASOLINE
STRAIGHT RUN GASOLINE
ALKYLATE
ALKYLATION
POLY
POLY PLANT
GASOLINE
DRY GAS
GASOLINE BLENDING PLANT
FUEL GAS
LP GAS
MOTOR GASOLINE
AVIATION GASOLINE
OLEFINS TO CHEMICAL
KEROSINE
LIGHT FUEL OIL
DIESEL FUEL
SULFUR
LUBES
WAXES
GREASES
HEAVY FUEL OIL
ASPHALT
COKE

Fig. 2-6. Processing plan for complete modern refinery.

2.2.2.1 Refinery Combustion Processes--Refinery heaters furnish the heat for distillation and cracking units and for other refining processes. Boilers supply steam for electric power generation, storage tank heating, and other process operations. Fuel requirements can be equivalent to 10 percent of the crude oil processed.[20]

More than half of the fuel requirements of a refinery is provided by the refinery; the balance consists of purchased fuels, primarily natural gas. Gases from distillation and cracking are common fuels, liquid low-value distillate and residual fractions are also burned, product-grade residual fuel oils are often used, and a significant number of refineries recover heat from fluid catalytic cracking regenerator gases in CO boilers. Although most petroleum coke is marketed, some may occasionally be used as a fuel. Also, combustion of acid sludges for acid recovery permits heat recovery. Fuel types consumed in the U.S. refineries during 1970 are shown in Table 2-7.[21] Nearly all of the sulfur in these fuels is oxidized to sulfur oxides during combustion.

Techniques in use for reducing the sulfur content of refinery gases and liquids are discussed in Section 4 and Section 3.3.2. Except for acid recovery plants used in conjunction with acid sludge burning (Section 2.2.2.7), stack gases from combustion processes are not now being desulfurized. It is possible, however, that the flue gas desulfurization processes discussed in Section 3.4 might be applicable for desulfurization of gases from refinery heaters and boilers.

2.2.2.2 Distillation--As illustration in Fig. 2-6, distillation is the first step in separating crude oil into its component parts. The crude is preheated and passed into a distillation or fractionating tower where the

Table 2-7. - ENERGY CONSUMED IN U.S. REFINERIES DURING 1970 BY FUEL TYPE

Fuel type	TJ
Fuel oil	282 500
Acid sludge	305
Liquefied petroleum gas	18 400
Petroleum coke	331 000
Refinery gas	1 045 000
Natural Gas	1 120 000
Coal	13 700
Purchased electricity	70 000
Purchased steam	31 400
Total energy	2 912 305

vapors of different boiling points condense, with the most volatile being collected at the top of the tower, nonvolatile residues at the bottom, and intermediate fractions between. Following atmospheric distillation, the heavier products can be separated further by vacuum distillation--a similar operation carried out at reduced pressure.

Although distillation separates crude into a number of fractions, most of these are not suitable for use without further refining. Even the more usable distillates, such as kerosene or light fuel oil, frequently contain corrosive sulfur compounds or objectionable odors and must undergo some type of desulfurization. Gases from atmospheric distillation units also contain sulfur compounds and are usually treated (Section 4) before being burned as fuel.

In vacuum distillation, jet exhausters are also potential emission sources. Although the volume is small, exhaust gases may contain as much as 25 percent H_2S by volume; these gases are also rich in hydrocarbon vapors and are usually flared to the atmosphere. Information on handling and emission control for these gases is given in Section 2.2.2.7.

2.2.2.3 Cracking--Cracking is a conversion process in which heavy hydrocarbon molecules are split into smaller molecules to increase the yield of gasolines and olefins. Gases produced by cracking processes vary in H_2S content depending on the process characteristics and the feed sulfur content; these gases are usually collected, desulfurized, and burned as fuel or are used in other refinery processes. Control techniques for refinery gases are discussed in Section 4.

The three primary cracking methods are thermal cracking, catalytic cracking, and hydrocracking. Thermal cracking is pressurized distillation; the plant is very similar to a distillation unit. Thermal cracking includes visbreaking, to reduce the heavy oils to a less viscous state, and coking, to transform heavy residuals into coke and into a distillate suitable for catalytic cracking or hydrocracking. Gases usually contain sulfur compounds. Also, unless the feedstock is of low sulfur content, sulfur compounds concentrated in the coke make it commercially undesirable. In delayed cokers where the coke accumulates at elevated temperatures, offgases contain almost 100 percent H_2S. Unlike delayed or fixed-type cokers, fluid-bed cokers (now in very limited use) recirculate smaller coke particles to the reactor through a burner, where heat is generated by burning part of the coke. These coke burners emit SO_2.

Catalytic cracking employs both high temperatures and chemical catalysts and has largely replaced thermal cracking. Catalytic crackers are generally of three types. The most popular is the fluid catalytic cracking (FCC) unit, in which a finely powdered catalyst is lifted into the reaction zone by the incoming oil and then into a regeneration zone by air. Following regeneration, the catalyst is recycled through the system. The second technique is the moving-bed method, typified by Thermofor catalytic cracking (TCC) and Houdriflow processes, in which a catalyst in granular or pelletized form is lifted by air or bucket elevators into the reaction zone and subsequently returned by gravity flow to the regeneration zone.[22] Also, there are fixed-bed systems in which the beds are alternately placed on-stream or in a regeneration cycle. Offgases contain as much as 10 percent H_2S. All of these methods require catalytic regeneration, which is accomplished essentially by burning off coke deposits. The regeneration process, particularly that associated with FCC units, is a major source of SO_2 emissions; it is discussed in Section 2.2.2.4.

Hydrocracking, a combination of catalytic cracking and hydrogenation, is used to supplement the FCC process. The reactions occur in the presence of high-pressure hydrogen in a fixed-bed reactor. Hydrogen suppresses the formation of heavy residuals and coke and thereby increases the yield of gasoline and light distillates. High-molecular-weight, sulfur-bearing hydrocarbons are also cracked, and the sulfur reacts with the hydrogen to form H_2S. Thus, process gas from the hydrocracker may contain as much as 25 percent H_2S.

2.2.2.4 Catalyst Regeneration--A catalyst loses its activity with use and must be either regenerated or replaced. In regeneration the coke that forms on the catalyst during cracking is oxidized to carbon monoxide by controlled combustion. Sulfur and sulfide deposits which also build up on catalysts are also converted to sulfur oxides during regeneration. Thus, catalytic regeneration is a significant source of SO_x emissions. The SO_x concentration may vary considerably depending on the amount of sulfur in the feedstock and on operating conditions. These gases are normally either vented directly to the atmosphere or flared or burned without desulfurization in CO boilers. Emission factors for catalyst regeneration are given in Chapter 6.

2.2.2.5 Reforming--Reforming, the rearrangement of atoms within a molecule (isomerization) and the removal of hydrogen atoms from the molecules (dehydrogenation), is used to convert cyclic paraffinic components of light petroleum fractions to aromatic hydrocarbons of much higher octane value. Catalytic reforming has virtually replaced thermal reforming and includes a number of different processes.[23] The most widely used process employs a platinum catalyst in a fixed bed. The catalyst has a relatively long life and does not require regeneration. Reforming produces excess hydrogen which is utilized in other processes (i.e., hydrotreating and desulfurization). The platinum-catalyst-reforming process is not a source of sulfur oxide emissions; only trace quantities of H_2S are present in the hydrogen by-product. Some SO_2 emissions may be associated with the regeneration of nonplatinum catalysts used in some other types of reforming operations not now in widespread use.

2.2.2.6 Polymerization and Alkylation--Polymerization is the combination of unsaturated hydrocarbon gases (olefins) into heavier fractions using phosphoric acid as a catalyst. Alkylation is fundamentally similar to polymerization except that only part of the charging stock need be unsaturated. Typically, an olefin is combined with an isoparaffin (in the presence of a catalyst such as sulfuric acid, hydrofluoric acid, or aluminum chloride) to increase molecular weight. Both of these processes are carried out in closed systems and have no significant impact on SO_2 emissions.

2.2.2.7 Miscellaneous Refinery SO_2 Sources

Air blowing of asphalt--Although residual asphalts are preferred for paving, blown asphalts are more desirable for roofing applications. Air blowing involves passing 480 to 530 K air (at a rate of about 20.9 $cm^3/s/kg$ over the charge in stills blanketed with steam[22] until the asphalt reaches the desired consistency. The effluent air from this process contains sulfur compounds, hydrocarbon gases, and aerosols.

Some asphalt oxidation units are equipped with afterburners, scrubbers, or packed fiber beds. Afterburners do not remove sulfur compounds. Although alkaline liquor scrubbers can be used for emission reduction, no useful information is available on such systems. Collection of these gases for fuel incurs the danger of explosion; but adequately engineered safeguards would permit the venting of these gases to a refinery heater or boiler equipped for flue gas desulfurization.

Vacuum jet exhausters--These units are used in the vacuum distilling process, in evacuating fixed-bed reactors prior to regeneration, and in removing hydrocarbon gases from process equipment during shutdowns.

The possibility of these exhaust gases being explosive complicates their use as fuel, but if barometric condensers are used, some scrubbing of sulfur compounds occurs. Other emission control possibilities are alkaline scrubbing (Section 3.4) and venting, with adequate safeguards, to heaters or boilers equipped with flue gas desulfurization systems

Waste acids and sludges--Acid sludge contains from 25 to 70 percent acid with the remainder consisting mostly of heavy hydrocarbons, alkyl sulfides, and thiophenes.[22] In most refineries waste acids and sludges are processed by acid manufacturing units.[24] Control techniques for sulfuric acid plants are discussed in Section 2.2.3.3.

Sour water strippers--Condensates, weak alkaline solutions, and other aqueous solutions from refinery processes are normally contaminated with H_2S. Sulfides are detrimental to natural waters and must be removed from effluent water streams. The most common procedure is to collect the stream in a closed system and strip the hydrogen sulfide with steam. The stripped H_2S can then be processed in a sulfur recovery system (Section 4), which is also a potential source of SO_2 emissions.

2.2.2.8 Refinery Desulfurization Processes--Methods of desulfurizing petroleum and refinery offgases include the following for converting sulfur to H_2S:

1. hydrogen treating
2. scrubbing with amino or other agents
3. distillate treatment

which are discussed in Section 4 of this report. The H_2S recovered may be processed in a sulfur recovery plant. Such facilities have become an essential part of refinery operations. The most widely used method, the Claus process, is also discussed in Section 4.

2.2.3 Sulfuric Acid Plants

Sulfuric acid is one of the largest volume industrial chemicals produced in the United States. Sulfuric acid production for 1971 was 20.9 Gkg for some 183 plants.

Production in the BRD in 1970 amounted to 3.28 Gkg.

The chief uses of sulfuric acid are in the production of fertilizer, manufacture of chemicals, oil refining, pigment production, iron and steel processing, synthetic fiber production, and metallurgical applications.

The basic processes used for the production of sulfuric acid are the contact process and the lead chamber process. Of the 183 U.S. sulfuric acid plants, 167, representing over 97 percent of the production, are contact plants.[25] The remainder use the older lead chamber process which is being phased out. No new chamber process plants are being built. For these reasons, control of sulfur oxides from lead chamber plants is not discussed. Eighty percent of the sulfuric acid plants in the BRD use the double-contact process.

About 68 percent of the contact-process sulfuric acid in the United States is produced from elemental sulfur. The remaining acid is made from iron pyrites (4.5 percent); tail gas from smelters (9 percent); and hydrogen sulfide, spent alkylation acid, and acid sludge from petroleum refineries (18.5 percent).[25] Table 2-8 gives production levels and sources for H_2SO_4 production in the BRD.

2.2.3.1 Process Description--Contact sulfuric acid plants are classified as either elemental-sulfur-burning plants or "wet-gas" plants. Wet-gas plants use such sources of sulfur as sulfur dioxide resulting from roasting of various copper, zinc, and other ore concentrates, from burning of spent

Table 2-8. - H_2SO_4 PRODUCTION IN THE BRD (1970)

Feedstock	Mkg SO_3
Elemental sulfur	462
Pyrites	1 800
Smelter tail gas	663
Other	156
Oleum	458
Total (approximate)	3 500

alkylation acids or hydrogen sulfide from refinery operations, from roasting of iron pyrites, and from recovery of SO_2 from copper converters and reverberatory furnaces.

A basic variation to the contact process is the double-contact, or dual absorption, process used for both elemental-sulfur-burning and wet-gas plants. The dual absorption process substantially reduces sulfur oxides emissions (Section 2.2.3.3).

Elemental-sulfur-burning process--Figure 2-7 is a schematic of an elemental-sulfur-burning plant. Sulfur is burned with excess air which has been dried in an absorber circulating 98-percent sulfuric acid to form a gas which contains from 8 to 11 percent sulfur dioxide. The SO_2 is oxidized to SO_3 in a converter with a catalyst. The oxidation of sulfur dioxide liberates heat which must be removed in boilers before additional oxidation can take place; thus several stages in the converter with intermediate gas cooling are required. The gas exiting from the converter is cooled in an economizer. The SO_3 is then absorbed in a circulating stream of 98-percent acid. The sulfur trioxide combines with the water in the

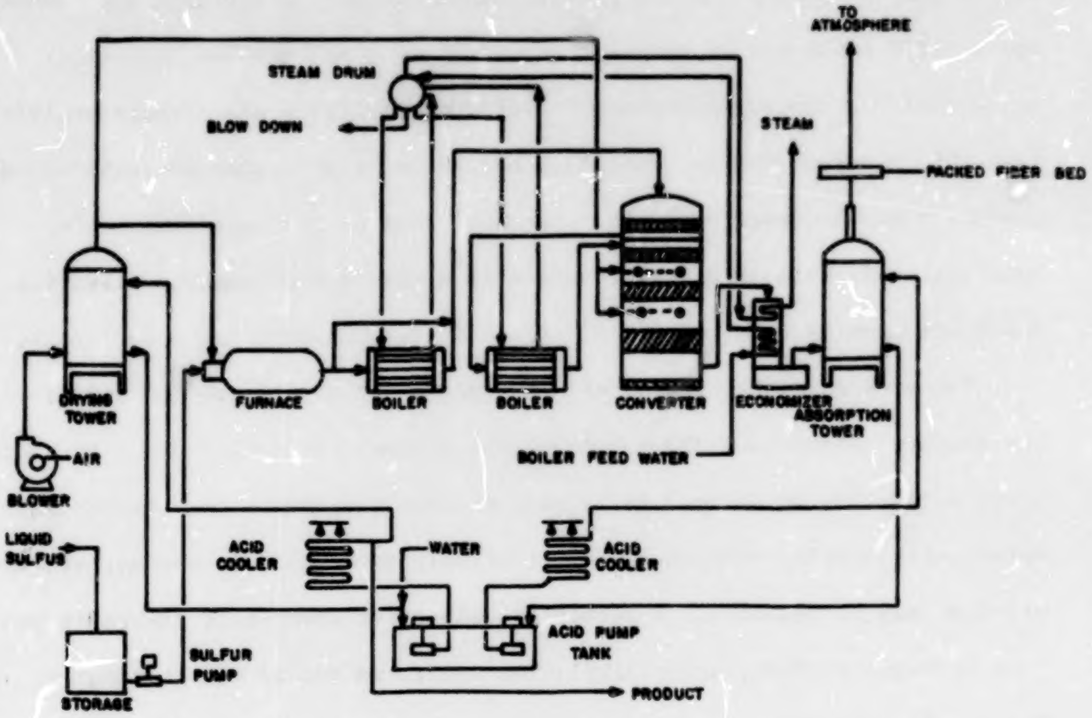

TO ATMOSPHERE
STEAM DRUM
BLOW DOWN
STEAM
PACKED FIBER BED
DRYING TOWER
FURNACE
BOILER
BOILER
CONVERTER
ECONOMIZER
ABSORPTION TOWER
AIR
BLOWER
BOILER FEED WATER
LIQUID SULFUR
ACID COOLER
WATER
ACID COOLER
ACID PUMP TANK
SULFUR PUMP
STORAGE
PRODUCT

Figure 2-7. Contact-process sulfuric acid plant burning elemental sulfur

acid to form additional acid, and water is, in turn, added to the acid to maintain the desired concentration.

If fuming sulfuric acid or oleum is produced, the sulfur-trioxide-containing gases are first passed through an oleum tower which is fed with acid from the 98-percent absorption system, and then the effluent gas from the oleum tower is passed through the 98-percent absorber for recovery of residual sulfur trioxide.

Wet-gas process--Wet-gas plants are more elaborate and expensive than sulfur-burning plants. These plants usually require additional gas-cleaning and cooling equipment to remove dust, acid mist, and gaseous impurities along with the excessive amounts of water vapor. When gas streams contain less than 8 percent sulfur dioxide, the larger sized equipment required to produce a given quantity of acid increases capital and operating costs. When sulfur dioxide concentrations are less than 3.5 percent, auxiliary fuels are usually required.

The process configuration of a wet-gas plant depends on the source of the sulfur. Figure 2-8 shows the overall process for such a plant burning spent acid. The spent acid is introduced into the combustion chamber and burned with undried atmospheric air. If only spent acid is burned, auxiliary fuel may be required. A common procedure for spent-acid plants is to burn hydrogen sulfide, spent alkylation acid, and sulfur simultaneously. The gas is then cleaned and cooled. From this point, the process is similar to an elemental-sulfur-burning plant.

2.2.3.2 Sulfur Dioxide Emissions--Figure 2-9 shows the relationship between the volumetric and mass sulfur dioxide emissions and the conversion efficiencies for various concentrations of sulfur dioxide at the converter inlet.

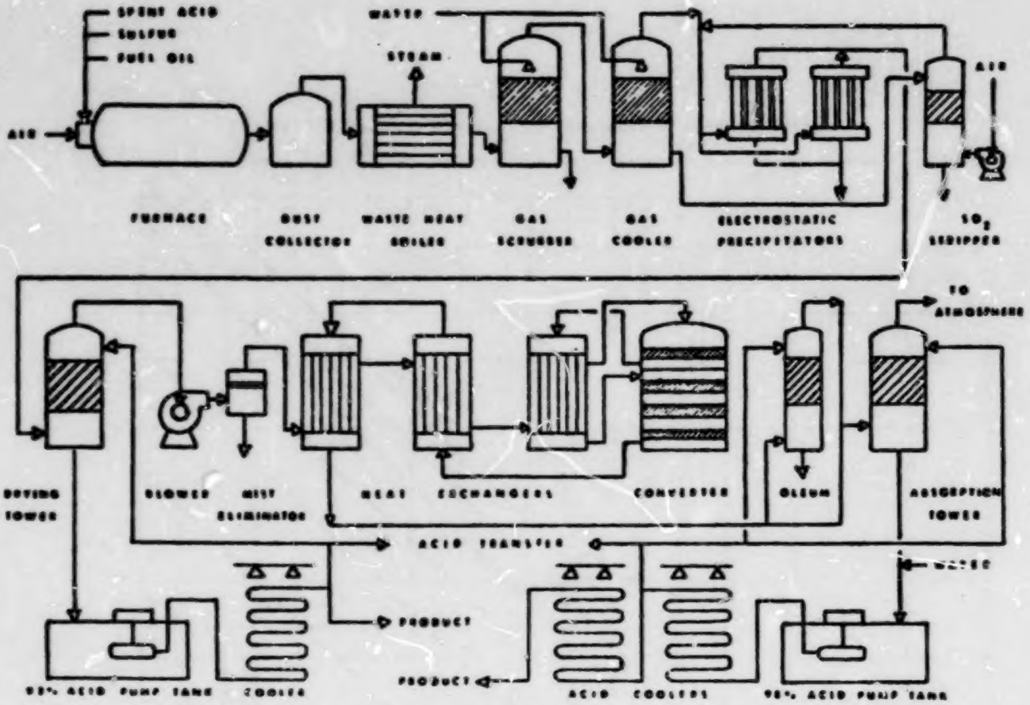

SPENT ACID
SULFUR
FUEL OIL
AIR
WATER
STEAM
AIR
FURNACE
DUST COLLECTOR
WASTE HEAT BOILER
GAS SCRUBBER
GAS COOLER
ELECTROSTATIC PRECIPITATORS
SO_2 STRIPPER
TO ATMOSPHERE
DRYING TOWER
BLOWER
MIST ELIMINATOR
HEAT EXCHANGERS
CONVERTER
OLEUM
ABSORPTION TOWER
ACID TRANSFER
WATER
PRODUCT
PRODUCT
93% ACID PUMP TANK
COOLER
ACID COOLERS
98% ACID PUMP TANK

Fig. 2-8. Contact-process sulfuric acid plant burning spent acid.

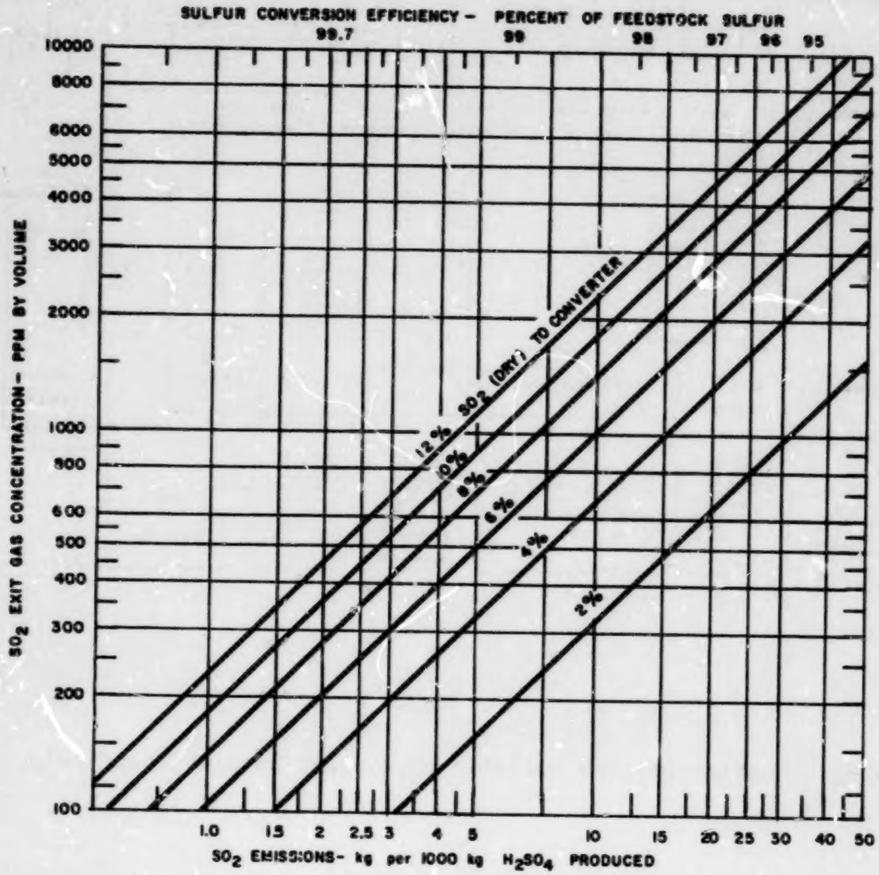


Fig. 2-9. Volumetric and mass SO_2 emissions at various SO_2 inlet concentrations and conversion efficiencies without air dilution

The conversion efficiency of either the single or the dual absorption contact process is improved through longer residence time of the reacting gases in the catalyst mass. This is achieved with larger reactors holding more catalyst. The catalyst, pelletized vanadium pentoxide, is separated into four or five fixed beds (or stages) in modern converters to maintain the optimum gas reaction temperature.

Plants built prior to 1960 have only three conversion stages and operate with about 95 to 96 percent conversion efficiencies. Plants built since 1960 have four or more converter stages with overall conversion efficiencies of between 96 and 98 percent. Typical sulfur dioxide emissions from various types of single-absorption plants without SO_2 tail gas recovery systems are shown in Table 2-9.[25]

Acid mist is also emitted from sulfuric acid plants. The quantity of acid mist formed depends on the strength of acid produced, the type of sulfur feedstock, and the absorption efficiency. Uncontrolled emissions average between 0.2 to 2 kg H_2SO_4 per 1 000 kg of acid produced for sulfur-burning plants that produce no oleum and about 0.5 to 5 kg/1 000 kg for spent-acid plants producing oleum. Additional information on acid mist emissions and control is presented in the document, Control Techniques for Particulate Air Pollutants.[26]

Sulfur dioxide emissions may exceed the normal emission rate during start-up or as a result of upset conditions. The frequency and duration of the abnormal emissions depend on the plant design, the type of control systems used, and the nature of the upset or startup problem.

The amount of SO_2 emitted during startup depends on how long it takes to bring all of the converter stages to the proper operating temperatures. If downtime has been several days or longer, the plant design and startup

Table 2-9. - UNCONTROLLED SULFUR DIOXIDE EMISSIONS FROM SINGLE-ABSORPTION SULFURIC ACID PLANTS WITH THREE- AND FOUR-STAGE CONVERTERS

	SO_2 in converter feed	SO_2 emissions			
		Three-stage converter		Four-stage converter	
		kg/1000 kg 100% acid	ppm by volume	kg/1000 kg 100% acid	ppm by volume
Sulfur	7.5-8.5	25-40	3 000-5 000	13-33	1 500-4 000
Hydrogen sulfide*	7.0	25-45	3 000-5 000	25-43	1 500-4 000
Acid sludge	6-8	25-43	2 500-4 000	15-21	1 500-5 000

*Also includes some other sulfur-containing compounds.

procedure may require from 1 to 24 hours to stabilize operations. For the first few hours, the emissions may be five times the normal rate if the final stage is not at the proper temperature before introduction of SO_2 to the converter. In many cases, the final stage can be raised almost to ignition by proper preheating with fuel oil or gas. The preceding stages are sufficiently heated to obtain nearly full conversion at reduced rates without the action of the last stage. Reaction heat then continues the heating process until ignition is obtained in the final bed.

Plants which have been down for shorter periods of time can stabilize operation in less time and with reduced probability that emissions will exceed the normal rate.

Certain preheating techniques can reduce the quantity of SO_2 emitted during startup if indirect catalyst heating is not available. Some plants use a two-step preheating sequence in order to bring the final catalyst bed to the proper temperature as quickly as possible. The first step brings the converter beds to a temperature well above the dewpoint, about 383 K, with dry air heating. The second step raises nearly all of the catalyst to ignition temperature, about 711 K, with hot fuel gas. In the first step, fuel oil or gas is burned with undried atmospheric air to heat the furnace and equipment ahead of the converter; the combustion gases are vented to the atmosphere until a predetermined exit gas or equipment temperature of about 1 366 K is reached; the burner is turned off, the vent closed, and dry air is blown through the furnace and the converter to heat the catalyst. Although one cycle is usually sufficient, this process must be repeated until the dewpoint temperature is exceeded. In the second step, the vent ahead of the converter is closed while the burner is reignited and operated until the last catalyst bed is nearly at ignition temperature, about 657 K. The first bed may reach 810 K at this time.

After the preheating sequence, sulfur or sulfur-containing feedstock is burned at a low rate using excess air to produce a weak SO_2 stream, which is fed to the converter. Some operators start feeding about 3 percent SO_2 at about 20 percent of full rate.

Adjustments are made to stabilize all operations, to bring all temperatures to normal conditions, and to increase gradually the feed rate and inlet SO_2 concentration as the temperature of the first bed decreases and as the last bed increases to ignition. Careful coordination of these adjustments is necessary to maintain stability and to prevent excessive SO_2 emissions. A careful operator may be able to prevent any violation of emission standards in plant startups.

Total emissions are reduced by running the plant at less than the usual production rate until proper operating temperatures can be attained. In this manner, even if the sulfur dioxide concentration (ppm) and the mass emission (kg/1 000 kg of acid) exceed the emission limit, the total amount of sulfur dioxide emitted during startup will be less than it would be if the plant were operated initially at full rate.

During routine operations, there are several types of upset conditions which can cause excessive emissions. Elemental-sulfur-burning plants have the fewest upsets because they operate with a constant concentration of sulfur dioxide to the converter. Plants using spent acid or some of the various metallurgical offgases are more prone to upset conditions. The most common operating problems which lead to excessive emissions are listed below:

1. sudden change in concentration of SO_2 to the converter in plants using spent acid or metallurgical offgases as feed,
2. oxygen starvation occurring in plants using roaster gas as feed,
3. equipment failure (e.g., pump or controller on absorber) causing excessive SO_3 emissions,
4. power failure.

Emissions are usually in the range of 50 to 100 percent higher than normal emissions for these types of upsets. From one-half hour to a few hours may be required to stabilize operations and emissions.

Upset conditions (e.g., heat exchanger leakage) can cause SO_2 to bypass the converter and generate higher emissions. These emissions usually build up gradually to the point where a plant shutdown in required. Because of the gradual buildup, such conditions can frequently be detected and corrected before emission standards are exceeded.

The rate and duration of abnormal emissions during an upset condition are dependent on the plant design and the sulfur oxide control process used.

For example, effluent gas desulfurization systems can be designed to accommodate the higher inlet concentrations for moderate periods of time. An example of the effect of the basic plant design is the modified heat exchanger configuration in use on the recently constructed dual-absorption plant built for Tomakomai Chemical Company in Tomakomai, Japan. This system enables the plant to accommodate wide swings in inlet SO_2 concentrations without upsetting the process. The plant was designed for a minimum conversion efficiency of 99.9 percent and a maximum tail gas concentration of 100 ppm of SO_2. Tests conducted at the plant while it was running at approximately half capacity showed emissions of 65 to 75 ppm.[27]

2.2.3.3 Sulfur Dioxide Control Methods--Sulfur dioxide emission control for sulfuric acid plants is well established. The dual-absorption process is operating successfully in over 90 plants throughout the world, including six plants in the United States. By early 1974, a total of 12 plants using various sulfur feedstocks are scheduled to be in operation in the United States. The dual-absorption process has been operating successfully in Europe for several years using various sulfur feedstocks.

In the dual-absorption process, as opposed to single-absorption, a greater fraction of the sulfur in the feedstock is converted to sulfuric acid. The SO_3 formed in the primary converter stages is removed in a primary absorption tower and the remainder is returned to the final stages. The resulting SO_3 is absorbed in a secondary absorption tower. At least 99 percent overall conversion of the sulfur dioxide to sulfur trioxide is obtained.

As shown in Figure 2-10, the dual absorption process requires the same types of equipment as the conventional single-absorber design. If dual

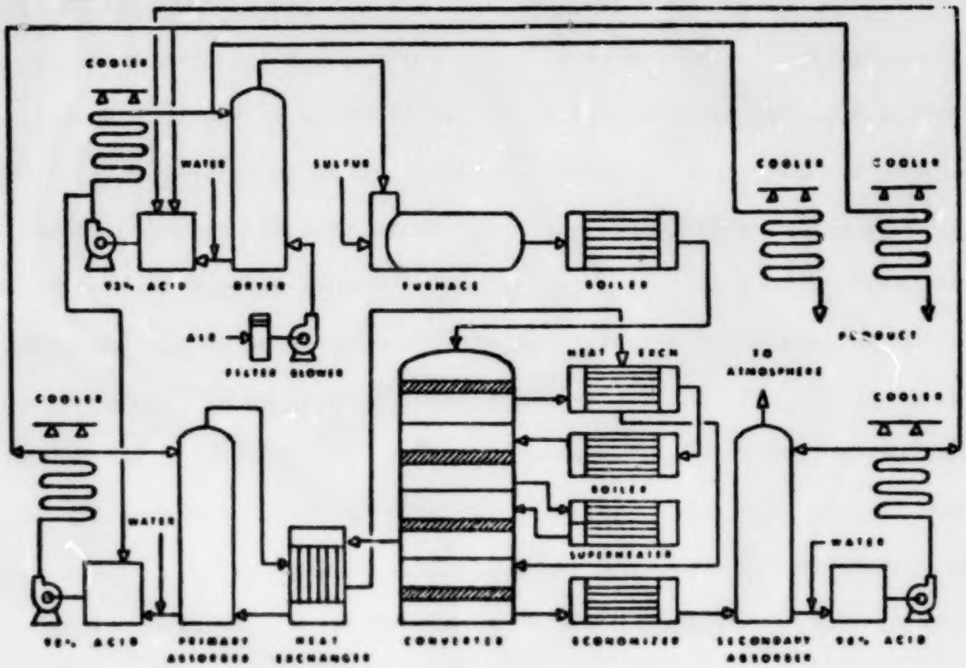

COOLER
WATER
SULFUR
93% ACID
DRYER
FURNACE
BOILER
COOLER
COOLER
PRODUCT
AIR
FILTER
BLOWER
HEAT EXCH
TO ATMOSPHERE
COOLER
COOLER
BOILER
WATER
SUPERHEATER
WATER
98% ACID
PRIMARY ABSORBER
HEAT EXCHANGER
CONVERTER
ECONOMIZER
SECONDARY ABSORBER
98% ACID

Fig. 2-10. Dual-absorption sulfuric acid plant.

absorption is added to existing single absorption plants, the heat necessary to reheat the gas exiting the primary absorber can be provided by either heat exchange with the converter gas, mixing in a small quantity of gas directly from the sulfur furnace, or by using an outside heat source.

Table 2-10 lists the sulfur feedstocks, related capacities, and maximum emission rates (design or test value, if available) for dual-absorption plants in the United States which are either on line or will be on line within the time shown.

In addition to the dual-absorption process, there are several desulfurization processes which are applicable to sulfuric acid plant effluent. These tail gas recovery systems, which are generally applicable to all classes of contact acid plants, can provide simultaneous control of SO_2, SO_3, and to some extent, acid mist. In the BRD, acid mist and SO_3 fumes have been successfully controlled by passage through packed fiber beds.[28] The processes which have the most potential for controlling sulfur oxides emissions from acid plants include sodium sulfite and ammonia solution scrubbing. These processes and others which may also have application to sulfur acid plants are discussed in Section 3.4.

Molecular sieve separation is also being offered for control of sulfuric acid plant emissions. This process may be suitable where sulfur oxides emissions must be controlled to low levels (i.e., 50 ppm or less).

Other control processes or process modifications, such as oxygen enrichment, to reduce or control emissions are still in the developmental stage and will not be further discussed.

Table 2-10. - STATUS OF DUAL-ABSORPTION SULFURIC ACID PLANTS IN THE UNITED STATES, 1972

Company	Plant location	Plant capacity 1000 kg/day	Feedstock	Conversion efficiency	Concentration		Emissions kg/1000 kg acid	Designer	Comments
					Inlet percent	Outlet ppm			
American Cyanamid	Linden, N.J.	630	Sulfur	99.5	10	500	<2.7	Monsanto	Operating since late 1970. Emission tests conducted at full capacity showed emissions ranging from 212 to 420 ppm.
American Smelting & Refining Company	El Paso, Texas	180-725	Copper converter gas	98.94-99.45	4-8	500	3.6-7.5	Wellman Power Gas	Scheduled startup, mid 1973.
Anaconda	Anaconda, Mont.	550	Copper converter gas	99	4.5	500	6.75	Wellman Power Gas	Scheduled startup, mid 1973.
Cities Service Columbian Div.	Monmouth Junction, N.J.	90	Combination of roaster gas & sulfur		8	100-500	<2.0	Monsanto	Manufacturing iron oxide pigments. Started operations July 1971.
Coastal Chemical	Pascagoula, Miss.	1 350	Sulfur	99.5	10	500	<2.75	Wellman Power Gas	Started operation January 1972.
Dept. of Defense	Joliet Army Ammunition Plant Joliet, Ill.	700	Spent acid	99.5	7-8.5	465	3.28	Monsanto	Scheduled startup, early 1973; stated emissions are maximum design values.
Dept. of Defense	Radford Army Ammunition Plant Radford, Va.	450	Spent acid & sulfur	99.5	7-8.5	500	<3.75	Monsanto	On line August 1972; measured SO_2 emissions were between 200 and 300 ppm with plant operating at 360 000 kg/day.
Inspiration Consolidated Copper Co.	Inspiration, Ariz.	1 200	Copper converter & electric furnace gas	NA	NA	NA	NA	Lurgi-Knost	
Kennecott Copper Corp.	Hayden, Ariz.	1 770 peak, 725 nominal	Combination of copper roaster & converter gas	99+	10.6	937	<4.75	Monsanto	Scheduled to be on line by end of 1973. Existing sulfuric acid plant converted to dual absorption.
ML Industries	St. Louis, Mo.	820	Sulfur	99.58	10	500	2.75	Wellman Power Gas	Designed to meet St. Louis Air Pollution Control Agency requirements. Started operation in mid 1971. Emissions stated are the maximum design values.
Standard Oil of California	El Segundo, Calif.	270	Spent alkylation acid, H_2S, & misc. acid treating		8	500	<3.6	Monsanto	Designed to meet LAAPCD regulations of <500 ppm. Scheduled startup, October 1972.
Texas Gulf Sulfur	Aurora, N.C.	1 400	Sulfur burning	NA	NA	NA	2.0	Monsanto	Scheduled startup in 1973.

NA = Information not available.
*kg SO_2 per 1 000 kg 100% H_2SO_4.

2.2.4 Iron and Steel Plants

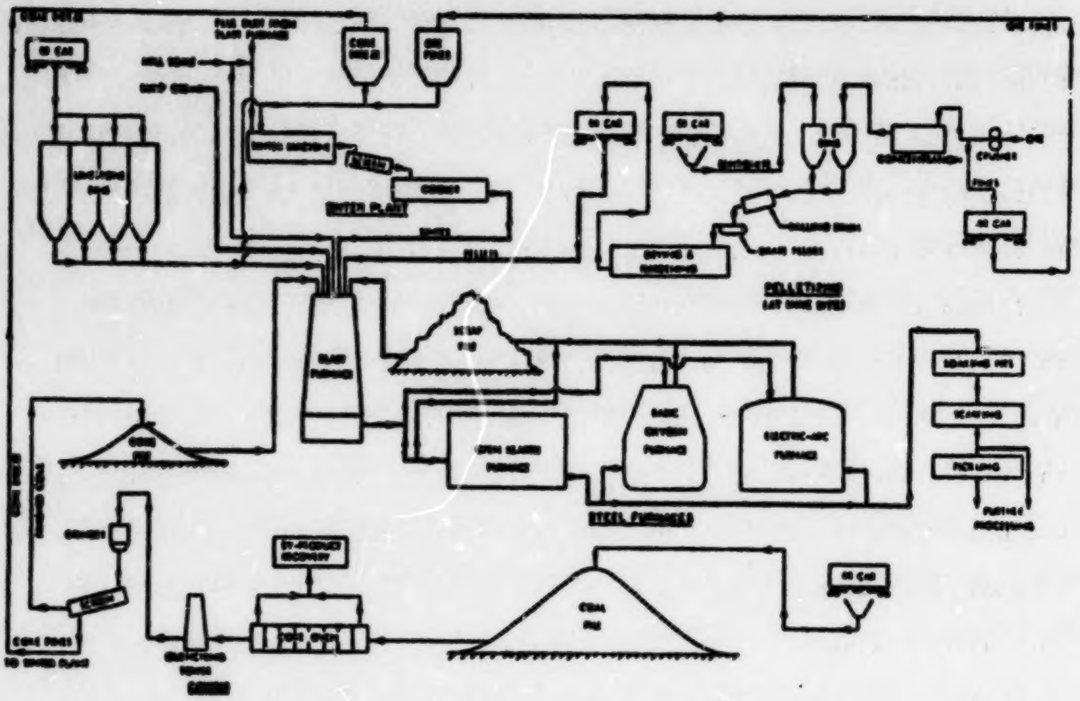
The primary processes at an integrated steelmaking facility are production of coke, reduction of iron ore to pig iron, and refining the pig iron into various grades of steel. These require a diversity of operations, as shown in the composite flow diagram, Fig. 2-11.

In the blast furnace, the combustion of coke provides the reducing atmosphere which converts the iron ore to metallic iron or pig iron. The pig iron is refined into steel by reducing the impurities and adjusting the alloy content to specified levels in open-hearth, basic oxygen, or electric arc furnaces.

Sulfur dioxide emissions are produced primarily from the sintering process and the combustion of coke oven gas. Some of the sulfur from the ore and coke is combined or trapped in the blast furnace and in open-hearth slags. As the slag cools and ages, some of this sulfur is released as H_2S or SO_2. The sintering and coke manufacturing processes, the associated sulfur dioxide emissions, and available control methods are discussed in the following sections. Methods suitable for controlling emissions from the various combustion operations are discussed in Section 3.4.

2.2.4.1 Sintering Machines

Process description--In the sintering process, iron ore containing fines, such as blast furnace flue dust, mill turnings, and mill scale, are mixed with limestone and a fuel, either coke breeze or coal, and burned to form a porous clinker suitable for use as a blast furnace feed. The sintering machine consists of an endless belt of cast steel pallets, which support the burning bed. The mixture of limestone, iron ore fines, and fuel is deposited on the pallets and ignited by gas or oil burners located near



RR CAR
SINTER PLANT
SINTER
PELLETS
PELLETIZING
(AT MINE SITE)
SCRAP PILE
BLAST FURNACE
COKE PILE
OPEN HEARTH FURNACE
BASIC OXYGEN FURNACE
ELECTRIC-ARC FURNACE
STEEL FURNACES
SOAKING PITS
SCARFING
PICKLING
FURTHER PROCESSING
BY-PRODUCT RECOVERY
COKE OVEN
COAL PILE
COKE FINES
TO SINTER PLANT
QUENCHING TOWER
COKING

Fig. 2-11. Composite flow diagram of an integrated steelworks.

the feed end of the unit. Once the coke breeze is ignited, combustion is self-sustaining. By the time the material is discharged from the pallets at the end of the sinter machine, the combustion front has moved through the bed forming the sinter. To provide for a reasonably uniform distribution of combustion air, the sections under the bed are separated into approximately 16 individual compartments called windboxes. A modern sinter plant has windbox discharge volumes of about 230 m^3/s.

Sulfur dioxide emissions--Approximately 1 kg of sulfur enters the sintering process per 1 000 kg of sinter produced. About half of this is in the iron-bearing material and the other half is in the coke, ignition fuel, and limestone. Approximately 35 percent of this sulfur ends up in the windbox gases as sulfur dioxide; the remainder is retained in the liquid slag formed in the combustion zone. The concentration of sulfur dioxide in the gases ranges from 50 to 100 ppm. The production of super-fluxed sinter, which uses additional limestone, substantially reduces the amount of sulfur dioxide emitted, since more sulfur is retained in the finished sinter;[29] but super-fluxing can increase particulate emissions. There are currently no plants which control sulfur dioxide emissions from the windbox gases.

2.2.4.2 Coking Ovens

Process description--Coke is the residue after the distillation of coal. The residue contains a high percentage of carbon and relatively small amounts of impurities.

In the byproduct coking process, which accounts for over 99 percent of the U.S. coke production, coal, which usually contains less than 1 percent sulfur, is heated in the absence of air in individual slot-type ovens. An individual oven is a narrow refractory channel, which may be up to 18 m long, 5.5 m high, and 510 mm wide. Usually 40 to 70 ovens are arranged side by side to form a coke oven battery. Some large batteries contain more than 150 ovens.

Flues between adjoining ovens are heated to produce the high temperature necessary to drive the volatile matter from the coal. Coal is charged through three to six ports in the top of an oven from larry cars, which are wide-gage vehicles fitted with coal hoppers that traverse the entire length of the battery.

Once an oven is fully charged, the charging ports are covered and sealed for the remainder of the coking cycle. The coke oven gases generated during the coking cycle are piped to a byproduct recovery section adjacent to the coke oven battery, where various byproducts, such as tar, ammonia liquor, and light oil, are recovered. These gases provide about 90 percent of the total underfiring energy.

During 1970, the underfiring of coke ovens consumed approximately 40 percent of the total coke-oven gas in the BRD. This accounted for 18 percent of total steel industry consumption of coke-oven gas.

At the end of the coking cycle, the incandescent coke is pushed out of the ovens into a special type of railroad car which conveys it to the quenching station.

Sulfur dioxide emissions--Approximately 25 to 35 percent of the sulfur present in the coal ends up in the coke oven gas. Virtually all of this is present as hydrogen sulfide. The normal range in 8 to 10 g/m^3. The typical hydrogen sulfide content is 9.6 g/m^3. A material balance on a typical coke oven shows 3.9 kg of sulfur contained in the coke oven gases generated during the production of 1 000 kg of coke.[29,30]

Use of the coke oven gas to underfire the coke ovens or as fuel for other combustion operations results in sulfur oxide emissions unless the hydrogen sulfide is removed. At integrated steel facilities, coke oven gas provides 70 percent of the total underfiring energy. Among merchant coke plants, coke oven gas is used almost exclusively. In 1968, the underfiring of coke ovens consumed approximately 35 percent of the total coke oven gas produced in any one plant and accounted for 26 percent of total steel industry consumption of coke oven gas.[30]

Although some plants strip the hydrogen sulfide from the coke oven gas, this practice is far from universal. It is generally practiced only where the gas is used in operations metallurgically sensitive to sulfur. There are some plants which convert stripped hydrogen sulfide to sulfuric acid for use in byproduct operations and pickling, but many of the plants simply vent or flare the H_2S.

Control Methods--Several processes (see Section 3) are suitable for removing hydrogen sulfide from coke oven gases. These processes either recover elemental sulfur or produce a concentrated stream of hydrogen sulfide which can be converted into sulfuric acid or elemental sulfur. The most commonly used in the first category are the Stretford, Takahax, and Fumaks processes. In the latter category are the Vacuum Carbonate and the Sulfiban processes.

The Takahax and Fumaks processes are similar in configuration to the Stretford process although the process chemistry differs significantly. These processes are being widely used in Japan with hydrogen sulfide removal efficiencies reported in excess of 99 percent. As with the Stretford process, these processes pose a potentially serious water pollution problem if the thiosulfate and thiocyanate are not removed prior to wastewater discharge.

2.2.5 Pulp and Paper Mills

Pulp and paper manufacture is one of the 10 largest industries in the United States. Per-capita demand for paper products was estimated at 252 kg in 1970.[31] The two phases of manufacture were pulping of wood and production of paper and its related products from the pulp. In the pulping process, wood is reduced to fiber, sometimes bleached, and then dried. Most pulp mills use a chemical cooking liquor to dissolve lignins and free the wood fibers and then recover the chemicals by some process involving combustion. Which pollutants--particulates, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, or sulfur dioxide--are emitted in significant amounts depends on the type of recovery process and the degree to which control equipment is used.

Three major pulping and recovery processes--namely, sulfate (kraft), sulfite, and neutral sulfite semichemical (NSSC)--account for nearly 80 percent of the pulp produced in this country. The other 20 percent is produced by specialized processes. Table 2-11 lists the processes, the quantity of pulp produced by each, and the potential atmospheric emissions.

Table 2-11. - POTENTIAL ATMOSPHERIC EMISSIONS FROM U.S. CHEMICAL PULP MILLS, 1970

Type of pulp process	Number of mills	Total 1970 production[a] Gkg	Major emission	Minor emission
Sulfate (kraft)	116	26.8	Particulates, odorous sulfides, and mercaptans	Sulfur dioxide
Sulfite	38	2.72	Sulfur dioxide	Particulates
Semichemical (NSSC)	50	3.26	Hydrogen sulfide	Particulates
Other[b]	12	1.54	--	--

[a] Air-dried.

[b] Includes soda pulp and dissolving mills.

The sulfate, or kraft, process has created the greatest air pollution problem, mainly because of the large quantity of visible particulates and the highly odorous nature of the sulfur compounds from pulp manufacturing.

2.2.5.1 Sulfate (Kraft) Process--Sulfate pulping involves cooking (digesting) wood chips in a solution of sodium hydroxide and sodium sulfide; sodium sulfate is the makeup chemical in the recovery process (Fig. 2-12). Upon completion of the cook, the residual pressure within the digester discharges the pulp into a blow tank. In the tank, pulp is diluted and pumped to washers where the spent chemicals and the organics from the wood are separated from the fibers. From the tank, gases and steam are vented through a condenser, and noncondensible gases, the sources of odors, are either confined and treated or released to the atmosphere.

The spent chemicals and the organics, called black liquor, are then concentrated in multiple-effect evaporators followed by direct-contact evaporators or forced to circulation concentrators for subsequent burning. A solids content of 60 to 70 percent in the black liquor is a requirement for combustion in the recovery furnace.

The concentrated black liquor is then sprayed into the recovery furnace, where the organic content supports combustion. The inorganic compounds, consisting of the cooking chemicals, fall to the bottom of the furnace where chemicals are withdrawn as a molten smelt, which is dissolved in a smelt-dissolving tank to form a solution called green liquor. The green liquor is pumped from the smelt-dissolving tank, treated with slaked lime, and then clarified. The resulting liquor, referred to as white liquor, is recycled to the digester.

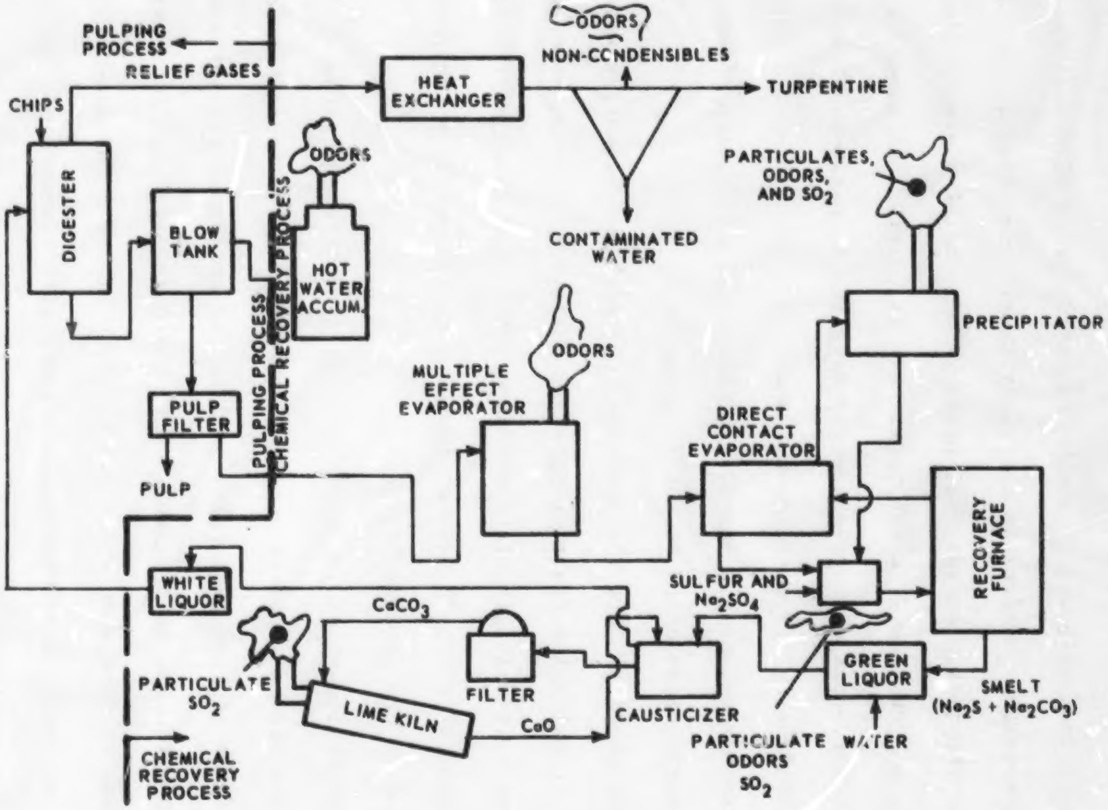

PULPING PROCESS
RELIEF GASES
CHIPS
DIGESTER
BLOW TANK
PULP FILTER
PULP
WHITE LIQUOR
PULPING PROCESS
CHEMICAL RECOVERY PROCESS
ODORS
HOT WATER ACCUM.
HEAT EXCHANGER
ODORS
NON-CONDENSIBLES
TURPENTINE
CONTAMINATED WATER
MULTIPLE EFFECT EVAPORATOR
ODORS
PARTICULATES, ODORS, AND SO_2
PRECIPITATOR
DIRECT CONTACT EVAPORATOR
RECOVERY FURNACE
SULFUR AND Na_2SO_4
GREEN LIQUOR
SMELT ($Na_2S + Na_2CO_3$)
WATER
PARTICULATE ODORS SO_2
CAUSTICIZER
FILTER
$CaCO_3$
CaO
LIME KILN
PARTICULATE SO_2
CHEMICAL RECOVERY PROCESS

Fig. 2-12. Typical kraft sulfate pulping and recovery process.

Sources of SO_2 are the recovery furnace, lime kiln, and smelt-dissolving tank. Boilers associated with the process may also emit SO_2 (see Section 2.1). Table 2-12 shows the estimated range of SO_2 emissions encountered in various sulfate mills.

Concentrations of SO_2 in recovery furnace exhaust gas range from less than 50 to 800 ppm. The factors responsible for this range are not well identified, but SO_2 emissions depend on: 1) cooking liquor sulfidity, 2) smelt bed depth, 3) manner in which liquor is sprayed into the furnace, 4) ratio of primary to secondary combustion air, and possibly 5) the furnace temperature.[33]

2.2.5.2 Sulfite Processes--Sulfite pulping is an acid-base process for dissolving lignin binding from wood chips. The bisulfite cooking liquor is produced by reacting SO_2, usually obtained from burning sulfur, with one of four bases (ammonium, calcium, magnesium, or sodium) in an absorption tower. During the cooking, the gases are vented occasionally as the pressure rises; these vent gases contain large quantities of SO_2 which are recovered for

Table 2-12. - RANGES OF ESTIMATED SO_2 EMISSIONS FROM KRAFT PROCESS[32]

Potential source	SO_2 emissions kg/1 000 kg air-dried pulp
Recovery furnace before DCE*	0.25 - 7.5
Recovery furnace after DCE*	0.25 - 4
Digester relief and blow	Trace - 0.005
Lime kiln	Trace
Multiple effect evaporators	0.0 - 0.05
BL oxidation tower	0.0 - 0.05
Brown stock washers	0.05 - 0.01
Smelt tank	0.0 - 0.05

*Direct contact evaporator

reuse into the cooking acid. As the cooked chips and spent liquor are discharged into a blow tank, water vapor and SO_2 escape to the atmosphere from the tank vent; and the pulp goes through a washing stage that separates the spent liquor from the fibers. The spent liquor is usually concentrated by evaporation and sprayed into a furnace where the organic compounds are burned, and the residual inorganic chemicals are collected for reuse in the manufacture of cooking acid.

Figure 2-13 shows a typical magnesium-base, chemical-digestion-and-recovery system with devices installed to control SO_2 and odorous sulfur compounds from the blow tank, multiple-effect evaporators, and recovery furnace. Table 2-13 presents typical emission ranges for the more common sulfite processes.

In the past, much of the spent sulfite cooking liquor has been sewered, but greater emphasis is being placed on burning the liquor, which is relatively high in organic sulfur content and a large potential source of SO_2, to reduce liquid effluent, recover chemicals, and generate steam. Control by scrubbing is possible, and recovered SO_2 can be used as makeup chemical.

Table 2-13. - ESTIMATED SO_2 EMISSION RANGES FROM SULFITE PULPING PROCESSES[32]

Process	SO_2 emissions kg/1000 kg air-dried pulp
Blow tank	
Hot blow	50 - 75
Cold blow	5 - 12.5
Evaporators	2.5 - 5
Recovery furnace	
Before scrubber	200 - 250
After scrubber	5 - 12.5

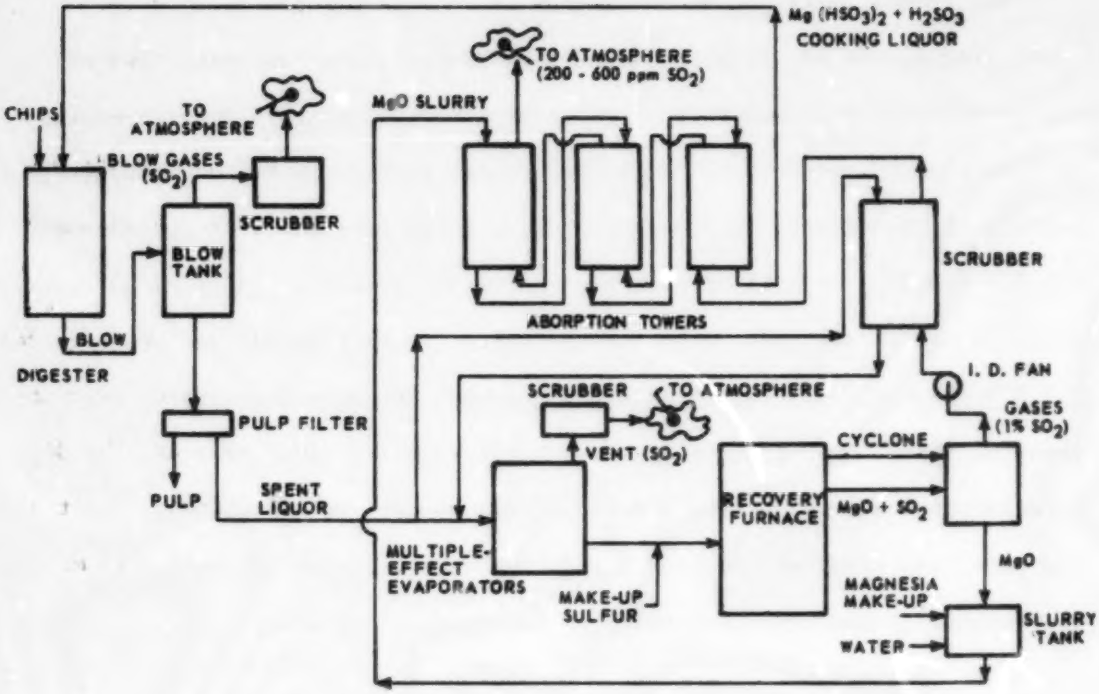

$Mg(HSO_3)_2 + H_2SO_3$
COOKING LIQUOR
TO ATMOSPHERE
(200 - 600 ppm SO_2)
MgO SLURRY
TO ATMOSPHERE
CHIPS
BLOW GASES
(SO_2)
SCRUBBER
BLOW TANK
BLOW
DIGESTER
ABORPTION TOWERS
SCRUBBER
I. D. FAN
GASES
(1% SO_2)
SCRUBBER
TO ATMOSPHERE
VENT (SO_2)
CYCLONE
PULP FILTER
PULP
SPENT LIQUOR
RECOVERY FURNACE
MgO + SO_2
MULTIPLE-EFFECT EVAPORATORS
MAKE-UP SULFUR
MgO
MAGNESIA MAKE-UP
SLURRY TANK
WATER

Fig. 2-13. Typical magnesium-base chemical pulping recovery process.

Since the magnesium and the SO_2 can be efficiently recovered, most new sulfite mills in the United States are of the magnesium-base type. Spent ammonium and calcium-base liquors can be burned, but only SO_2 can be economically recovered; the ammonia is destroyed, and calcium sulfate has no reuse value. Burning sodium-base liquors produces sodium sulfate and sodium carbonate for use as makeup chemicals in a draft process.

Economical operation of the magnesium sulfite process requires efficient recovery of SO_2 from the combustion gases, since concentrations of over 1 percent SO_2 (10,000 ppm) result from liquor combustion. If recovery is less than 90 percent, SO_2 emissions can be as high as 30 kg/1 000 kg of pulp; with 90 percent, they can be reduced to approximately 10 kg/1 000 kg (10 000 ppm);[34] over 98 percent recovery with three-stage venturi absorption can reduce SO_2 stack emissions to about 1.5 kg/1 000 kg (1 500 ppm).[35]

2.2.5.3 Neutral Sulfite Semichemical Process--The neutral sulfite semichemical (NSSC) pulp process, the most widely used semichemical process, normally uses sodium sulfite and sodium bicarbonate as a cooking liquor. The name "semichemical" is used because the cementing or lignin material is not completely removed chemically, so some mechanical disintegration is required to separate the fibers.

During cooking, steam maintains the temperature and pressure within certain limits, depending on the end use of the pulp, and odorous gases are created. At the completion of the cooking, residual pressure discharges the entire contents from the batch digester into a blow tank, and waste gases are vented to the atmosphere through an accumulator.

Then the pulp fibers are washed, usually on multistage drum filters. If no kraft process is available, the waste liquor is treated and sewered;

and if chemical recovery is not practiced, additional sulfur is added to the process via burning. If a kraft system is adjoining, a limited percentage of the NSSC spent liquor can be mixed with the spent kraft liquor and burned in the recovery furnace. The recovered chemicals are used entirely in the kraft system.

Sulfur dioxide is emitted from the recovery furnace (if used), from the digester and blow tank, from the sulfiting absorption tower, and from the stock washers. Emissions of both SO_2 and hydrogen sulfide may be increased from the kraft recovery furnace when NSSC liquor is added. Quantitative emission data from NSSC plants are not available and would vary widely depending on the type of recovery.

2.2.5.4 Steam and Power Boiler Atmospheric Emissions--Many pulp and paper mills have auxiliary power boilers to produce process steam. When these units are fired by coal or residual oil, SO_2 emissions can be quite significant (Table 2-14), larger, in fact, than any SO_2 emissions from chemical recovery processes.

Table 2-14. - EXAMPLES OF SO_2 EMISSIONS FROM STEAM AND POWER BOILERS

Fuel	Emission kg of SO_2 per 1000 kg of fuel
Bark	1 - 1.5
Oil (2 percent sulfur content)	35 - 40
Coal (2 percent sulfur content)	35 - 40
Natural gas	Trace

2.2.6 Waste Disposal

Disposal of coal refuse, solid wastes, and sewage can cause sulfur oxide pollution problems.

2.2.6.1 Coal Refuse--Coal refuse, also referred to as culm or reject materials, consists primarily of a mixture of coal, rock, carbonaceous shales, and pyrites. These materials, which accumulate during coal mining and cleaning operations, are disposed of as economically and as conveniently as possible. They are frequently used as construction fill for roads and building sites in coal-producing areas as well as for backfilling in mined areas to control subsidence. Coal refuse disposal sites sometimes become dumping grounds for discarded grease-soaked rags, grease and oil containers, trash and garbage from nearby homes, wood, and other organic matter. Depending on the local geologic formation and the local mining and preparation methods, the combustible content of coal refuse piles can vary from 10 to 60 percent.[36]

Coal refuse banks can be ignited by spontaneous combustion, accidents of nature (such as lightning and forest fires), or by humans, either accidentally or intentionally. Spontaneous combustion is probably the major cause of coal refuse fires. Of the 292 refuse banks found burning in 1968, 66 percent are believed to have started from heat generated within the pile.[37]

Because of the emission of sulfur oxides and other toxic gases, burning and smoldering coal refuse banks are air pollution sources. It has been estimated that 128 Mkg of SO_x were emitted to the atmosphere during 1970 from 266 Gkg of burning coal refuse.[2] Air samples taken in communities having burning coal refuse piles have shown SO_2 concentrations averaging more than 1.0 ppm with maximum peak concentrations exceeding 4.5 ppm.[37] Hydrogen sulfide concentrations exceeding 0.4 ppm have also been measured.[38] Methods for controlling these emissions are discussed in Section 3.5.

2.2.6.2 Solid Wastes--Incineration is a controlled combustion process for converting solid wastes to gases and to a residue containing little or no combustible material. Municipal incineration involves combustion of such materials as paper, wood, foliage, garbage, rubber, glass, rock, metals, and the like, which are usually generated in homes, businesses, and small industries.[39] Incinerators that handle pathological wastes or specialized trade wastes (such as sawdust, chemical sludges, etc.) are commonly referred to as onsite incinerators. Sewage sludge may also be incinerated (Section 2.2.6.3).

During incineration, moisture is evaporated, and the combustible portion of the solid waste is vaporized and then oxidized. Concurrent reactions include the oxidation of metals and such elements as sulfur and nitrogen. The major end products of municipal waste incineration are carbon dioxide, water vapor, ash, and various noncombustibles. Municipal incinerators discharge particulate matter and lesser amounts of other contaminants such as sulfur oxides, nitrogen oxides, hydrocarbons, hydrogen chloride, metals, and metal oxides.[39] Onsite incinerators may have similar or completely different emission characteristics depending on the incinerator feed.

On the average, municipal refuse contains about 0.1 percent sulfur. Sulfur compounds, usually in the form of sulfates and sulfides, are present chiefly in paper, food waste, garden waste, and rubber. During incineration, some of these compounds are converted to sulfur dioxide and possibly some sulfur trioxide as well.[39] If the average sulfur content is converted to SO_2, about 2 kg of SO_2 are emitted per 1 000 kg of refuse burned.[40] This value is slightly higher than that measured at 13 incinerators; there, the average value was 1.16 kg of SO_2 per 1 000 kg of refuse with a standard deviation of

0.88 kg per 1 000 kg.[40] During 1970, total SO_2 emissions were 13.6 Mkg for municipal incinerators and 31 Mkg for onsite incinerators.[2] However, these estimates may be low since they were based on an emission factor of 0.75 kg of SO_2 per 1 000 kg. With little or no controls, SO_2 emissions from incinerators are projected to be about 145 Mkg per year by the year 2000.[41]

Current and projected incinerator SO_2 emissions represent less than 1 percent of national sulfur oxide emissions. In fact, the sulfur content of municipal refuse is so low in comparison with that of many fuels that some consideration is being given to the use of refuse itself as a fuel.

At present, control of SO_2 emissions from incinerators is not being practiced. Some of the flue gas desulfurization processes discussed in Section 3.4 may be effective for incinerator stack gases if SO_2 emission controls become desirable.

2.2.6.3 Sewage--Although many sewage treatment operations result in odors and various other gaseous byproducts, there are only two sources of SO_2 emissions: the combustion of sludge digester gases and incineration of sludge.

The simplest sludge digesters are basically storage tanks where the sludge is held sufficiently long to undergo partial or complete digestion. The more advanced designs provide for tank heating and gas collection. Although sludge digester gas is composed primarily of methane (a combustible) and carbon dioxide, it also frequently contains hydrogen sulfide. Then digester gases are burned as fuel, the hydrogen sulfide is converted to SO_2. Hydrogen sulfide concentrations at most treatment plants are within 2.3 g/m^3 of gas;[42] however, concentrations as high as 14 g/m^3 have been reported where high-sulfate water has entered the sewer.[43] Control methods are discussed in Section 3.5.

2.2.7 Miscellaneous Sources

There are several manufacturing operations, limited in geographical distribution and scale of production, which are actual or potential sources of SO_2 emissions. There is little published information from which to estimate emissions quantitatively for these industries.

Sulfur oxide emissions discussed for the following miscellaneous sources are in addition to emissions from fuel combustion sources.

2.2.7.1 Glass Manufacture--Sulfur dioxide emissions may occur from the use of salt cake (Na_2SO_4) in the glass tank charge and from use of fuel in the melting furnace. Soda ash, sand, lime, and powdered coal are among the substances charged.[44] The following reaction involving sulfur dioxide takes place:

$$Na_2SO_4 + nSiO_2 + C \rightarrow Na_2O \cdot nSiO_2 + SO_2 + CO .$$

No control of gaseous emissions is generally practiced.

2.2.7.2 Corn Starch Production--In a typical wet-milling process, corn kernals are steeped in water containing 0.2 percent SO_2 at 322 K for 48 hours. This steeping prepares the kernels for separation into starch, gluten, and fibers. Sulfur dioxide is the most effective and most widely used reagent for this purpose. Although no control of emissions is usually practiced, scrubbers have been used in some cases to reduce emissions.

2.2.7.3 Sugar Manufacture--Lime is added to syrup during the sugar manufacturing process to precipitate certain undesirable impurities. Calcium ions in the remaining solution are precipitated by bubbling SO_2 through the syrup to form calcium sulfite. Minor emissions of SO_2 can occur, depending on plant design and operation.

2.2.7.4 **Sulfur Fusion Processing**--Processing of batches of sulfur by fusion can emit sulfur oxides at low levels whenever the fusion vessel or kiln is opened. An example is the manufacture of ultramarine by fusing kaolin, charcoal, sodium carbonate, sulfur, quartz, sodium sulfate, and resin. The melt is removed from the kiln, cooled, ground, and washed. The insoluble compounds are then heated with more sulfur to 780 K until a blue color develops.

2.2.7.5 **Liquid Sulfur Dioxide Production**--The national output of liquid SO_2 in 1967 was 98.3 Mkg.[45] The gas is produced by burning sulfur or by roasting metal sulfides. The cooled gases containing up to 18 percent SO_2 are sent to a water absorber.[44] The SO_2 is stripped from the water, cooled, dried, compressed, and liquefied. About 0.02 percent of the total SO_2 is lost into the atmosphere.

2.2.7.6 **Silicon Carbide Production**--Silicon carbide, an important abrasive, is made in an electric furnace at temperatures of 2 500 K using sand and coke as raw materials.[44] The furnace has no top, and its walls are temporary so that they can be torn away from the charge after completion of heating. Gases generated go directly to the atmosphere. The unreacted materials are later separated from the product and recycled as fresh furnace charge.

Any SO_2 evolved in this process is from the oxidation of sulfur in the coke. About 1.4 kg of coke are charged per kg of carbide produced.

2.2.7.7 **Titanium Dioxide Production**--In the manufacture of titanium dioxide by the sulfuric acid process, the acid added in batches to titanium ore in a digester yields primarily titanium sulfate and ferrous sulfate. The digester products are washed and separated. The ferrous sulfate goes to waste. The titanium compounds enter a calciner, where they are heated and converted to titanium dioxide. Sulfur trioxide and sulfuric acid mist are emitted from the calciner. On the basis of limited field test data, about 20 kg of SO_2 are emitted per 1 000 kg of calcined titanium oxide.

2.2.7.8 Organic Sulfonation--A large number of organic compounds, especially aromatics, are sulfonated by the addition of sulfuric acid. These are generally batch-type reactions in vented reactors. Emissions of sulfur dioxide are due to the excess sulfuric acid used to force the reaction to completion. Emissions may not be in large amounts, but they are sometimes very concentrated. Packed scrubbers containing a basic solution can reduce emissions.

REFERENCES FOR CHAPTER 2

1. Stern, H. C. Air Pollution (2nd edition), Vol. III, Academic Press, 1968.
2. OAP Data File of Nationwide Emissions 1970, National Air Data Center, Applied Technology Division, July 1972.
3. Kohlenabsatzstatistik (Steinkohlen) Statistik der Kohlenwirtschaft e.v., Essen.
4. Stat. Jahrbuch 1971, Stat. Bundesamt, Wiesbaden.
5. Studie "SO_2 Emission in der BRD für das BMI, NUKEM.
6. Perry, John H. (Ed.). Chemical Engineers' Handbook. McGraw-Hill Book Company, Inc., New York, Fourth edition. 1963.
7. MWV Jahresbericht 1971, Hamburg.
8. Gasversorgung und Umweltschutz. H. Pichler, H. Driesen, gwf 113/72/2.
9. Danielson, John A. (Ed.) Air Pollution Engineering Manual. U.S. Dept. of Health, Education, and Welfare, Cincinnati, Ohio. 1967.
10. Systems Study for Control of Emissions, Primary Nonferrous Smelting Industry. Arthur G. McKee & Company. Final report to National Air Pollution Control Administration, Contract PH 86-65-85, June 1969.
11. Ivor E. Campbell and James E. Ford. Sulfur Oxide Control at the Copper Smelter. Presented at the Second International Lime/Limestone Wet Scrubbing Symposium. New Orleans, La., Nov. 8012, 1971.
12. Konrad T. Semrau. Control of Sulfur Oxide Emissions from Primary Copper Lead, and Zinc Smelters--A Review. Presented at 63rd Annual Meeting of the Air Pollution Control Association, St. Louis, Mo., June 14-18, 1970.
13. New Source Performance Standards - Technical Report - Copper, Lead, and Zinc Smelters. EPA, Office of Air Programs, Research Triangle Park, N.C., October 1972.
14. Economic Impact of Anticipated Pollution Abatement Costs on the Primary Copper Industry - Part II. Arthur D. Little, Inc. Draft report to EPA, May 1972.
15. D. W. Rodloff and E. R. Marble, Jr. "Inspiration's New Look," Journal of Metals, July 1972, pp. 14-24.
16. Control of Sulfur of Oxide Emissions in Copper, Lead, and Zinc Smelting. U S. Bureau of Mines Information Circular 8527, Washington, D.C., 1971.

17. Oil and Gas Journal, "Annual Refining Issue," March 27, 1972.

18. Laster, L. L. "Air Pollution Aspects of the Petroleum Refinery Industry," Memorandum, Control Systems Division, EPA, December 1971.

19. Chemical Economy and Engineering Review, Vol 2, No. 5, pp. 19-21, May 1970.

20. Petroleum Refinery Background Information for Establishment of Federal Standards of Performance for Stationary Sources. Final Report prepared for OAP, EPA by Processes Research, Inc., Cincinnati, Ohio, June 11, 1971.

21. Mineral Industry Surveys, Annual Petroleum Statement (1970). Bureau of Mines, Washington, D.C., December 23, 1971.

22. Henstebeck, R. J. Petroleum Processing Principles and Applications, McGraw-Hill, New York, 1959.

23. Nelson, W. L. Petroleum Refinery Engineering, McGraw-Hill, New York, 1958.

24. Elkin, H. F., and Constable, R. A. "Control of Air Pollution in Petroleum Refineries," presentation at the U.S. Environmental Protection Agency-Institute of Chemical Engineers Conference, San Juan, Puerto Rico, July 17, 1971.

25. Current Industrial Reports, Series M28A, Bureau of the Census, U.S. Department of Commerce.

26. Control Techniques for Particulate Air Pollutants. Draft of Second Edition prepared for NATO Committee on the Challenges of Modern Society. November 1972.

27. Private communication: Mr. Timothy Browder of Ralph M. Parson Company, Los Angeles, Calif., Sept. 18, 1972.

28. Chemische Industrie 7/Juli 1970, Vol. 22, Nr. 7. Abgas reinigung in Schwefel-und Schwefel säurenanlagen mit Faser-Nebel abscheider. J. A. Brink, W. F. Burggrabe, L. E. Greensell--Monsanto.

29. Varga, J., and Lownie, H. W. "A System Analysis Study of the Integrated Iron and Steel Industry." Battelle Memorial Institute. Prepared for the National Air Pollution Control Administration, Contract No. PH 22-68-65, May 15, 1969.

30. Barnes, T. M., Hoffman, A. O., and Lownie, H. W. "Evaluation of Process Alternatives to Improve Control of Air Pollution from Production of Coke." Battelle Memorial Institute. Prepared for National Air Pollution Administration, Contract No. PH 22-79-75, January 31, 1970.

31. "Air Pollution Aspects of Pulp and Paper Manufacturing Industry." EPA, December 1972.

32. Hendrickson, E. R., Roberson, J. E., and Koogler, J. B. "Control of Atmospheric Emissions in the Wood Pulping Industry." Final Report on Contract No. CPA 22-69-18, Environmental Engineering, Inc., Gainesville, Fla., March 15, 1972.

33. Blue, J. D., and Lewelyn, W. F. "Operating Experience of a Recovery System for Odor Control." TAPPI, 54(7):1143-1147, July 1971.

34. Hanway, J. E., Henby, E. B., and Smithson, G. R., Jr. "Magnesium-Base Cooking Liquor Preparation by Absorption of Dilute Sulfur Dioxide in Flooded-Bed Towers." Preprint. (Presented at 1966 Alkaline Pulping Conference, TAPPI, Richmond, Va., Sept. 13-16, 1966).

35. Clement, J. L. "Magnesium Oxide Recovery Systems. TAPPI, 49(8):127A-134A, August 1966.

36. Flegal, R. C., and Gahr, N. J. "A Summary Report on Demonstration Methods for Extinguishing Culm-Bank Fires," Office of Air Programs, EPA, November 1971.

37. McNay, L. M. "Coal Refuse Fires, An Environmental Hazard," Information Circular 1515, Bureau of Mines, Department of the Interior, 1971.

38. Sussiman, V. H., and Mulhern, J. J. "Air Pollution from Coal Refuse Disposal Areas," J. Air Pollution Control Assoc., 14(7):279-284, 1964.

39. "Control of Air Pollution from Municipal Incinerators." Rough Draft, Office of Air Programs, EPA, Durham, N.C., August 1971.

40. Systems Study of Air Pollution from Municipal Incineration. A. D. Little, Inc., V-49--V-54.

41. Niessen, W. R., Sarofim, A. F., Mohr, C. M., and Moore, R. W. "An Approach to Incinerator Combustible Pollutant Control," 1970 ASME Incinerator Conference.

42. Norris, H. E. "Scrubbing Sewage Gas," Water Works and Sewerage, 90(2):61, February 1943.

43. Buswell, A. M. "Gas Scrubbing for H_2S Removal and Methane Enrichment," Public Works, 92(3):112-114, 198, March 1961.

44. Shreve, R. N. (Ed.). Chemical Process Industries. McGraw-Hill, New York, 1967.

45. 1967 Census of Manufacturers. U.S. Dept of Commerce, Bureau of the Census.

3. CONTROL METHODS

3.1 ENERGY SOURCE SUBSTITUTION

Substitution of energy sources with less potential sulfur oxide emissions for high-sulfur sources is one of the methods presently used to reduce sulfur oxide emissions. Thus, utilization of nuclear fuel or hydropower for electrical generation or substitution of low-sulfur coal or oil for high-sulfur fuels can significantly reduce sulfur oxide emissions.

Although energy source substitution is simple to understand with respect to the effectiveness of emission control, it is most complex to apply as a control technique. This is because the application of energy source substitution involves and affects conservation, national economy, national security, and foreign relations. This section is limited to presentation of information on the various energy sources as a basis for development and evaluation of air pollution control strategies rather than as a suggestion or recommendation of solutions for the serious and complex problems involved.

The reduction of sulfur oxides emissions effected by the substitution of low-sulfur fuels is substantially equivalent to the reduction in fuel sulfur content as estimated in Section 2.3.

Estimates of 1971 U.S. energy consumption and uses are illustrated in Figure 3-1.[1]

The following sections on energy resources note the sulfur contents of the basic fuel sources and the factors affecting availabilities.

3.1.1 Coal

Coal is the only fossil fuel with sufficient proven reserves to meet energy demands for both the short- and long-term projections, but the supply of low-sulfur coal of high rank is somewhat limited. The estimated recoverable reserves of coal by sulfur content are shown by region in Table 3-1.

Table 3-1. - U.S. COAL RESERVES AND RECOVERABLE RESERVES (JAN. 1, 1965)
(IN Gkg)

REGION	COAL RANK	TYPE RESOURCE	SULFUR CONTENT (BY WEIGHT - DRY BASIS) <0.7	0.8-1.0	1.1-1.5	1.6-2.0	2.1-2.5	2.6-3.0	3.1-3.5	3.6-4.0	>4.0	TOTAL	% REC. RES. TO TOTAL RESERVES
NORTHERN APPALACHIAN	BIT.[1]	RES.[2]	41	2,499	19,363	20,906	24,965	10,839	7,963	6.490	725	93,811	13%
		REC. RES.[3]	4	327	2,521	2,716	3,247	1,406	1.034	844	95	12,195	
SOUTHERN APPALACHIAN	BIT.	RES.	33,808	37,210	16,448	8,970	2,512	3,184	249	41	77	102,500	
		REC. RES.	3,719	4,091	1,809	989	277	349	27	4	9	11,274	11%
EASTERN INTERIOR	BIT.	RES.	177	1,229	9,138	8,285	6,748	29,296	60,828	78,687	32,221	226,609	
		REC. RES.	45	308	2,286	2,072	1,687	7,324	15,206	19,673	8,054	56,656	25%
WESTERN INTERIOR	BIT.	RES.	227	698	2,245	1,070	8,317	1,877	10,285	26,280	56,855	107,856	
		REC. RES.	18	54	181	86	667	150	821	2,104	4,630	8,530	8%
NORTHERN ROCKIES	BIT.	RES.	5,691	6,181	186	358	363	159	36	23	535	13,532	
		REC. RES.	626	680	18	41	41	18	4	0	59	1.487	11%
NORTHERN ROCKIES	SUB.[4]	RES.	117,606	98,904	0	1,179	0	0	0	0	9	217,698	
		REC. RES.	12,938	10,879	0	132	0	0	0	0	0	23,949	11%
SOUTHERN ROCKIES	BIT.	RES.	35,318	51,060	0	1,383	0	0	0	0	3,623	91,385	
		REC. RES.	3,533	5,106	0	136	0	0	0	0	363	9,138	
SOUTHERN ROCKIES	SUB.	RES.	47,214	15,337	136	0	0	0	0	0	0	62,6[illegible]	
		REC. RES.	4,721	1,533	14	0	0	0	0	0	0	6,267	10%
WEST COAST	BIT.	RES.	816	621	0	0	0	0	0	0	0	1,437	
		REC. RES.	73	54	0	0	0	0	0	0	0	127	8%
WEST COAST	SUB.	RES.	3,428	531	0	0	0	0	0	0	0	3,959	8%
		REC. RES.	308	45	0	0	0	0	0	0	0	354	
TOTAL BITUMINOUS AND SUBBITUMINOUS		RES.	244,328	214,270	47,536	42,153	42,906	45,355	79,363	111,520	94,047	921,476	
		REC. RES.	25,986	23,079	6,830	6,172	5,918	9,247	17,092	22,625	13,129	130,077	
TOTAL ANTHRACITE (OVER 95% IN PA.)		RES.	11,383	86	0	132	258	0	0	0	0	11,859	11% (THE N. APP. FACTOR)
		REC. RES.	1,478	9	0	18	32	0	0	0	0	1,537	
TOTAL LIGNITE (OVER 98% IN NORTHERN ROCKIES)		RES.	312,570	55,676	37,337	0	0	422	0	0	0	406,005	11% (THE N. ROCKIES FACTOR)
		REC. RES.	34,380	6,122	4,109	0	0	45	0	0	0	44,656	

[1] BITUMINOUS; [2] KNOWN RESERVES; [3] KNOWN RECOVERABLE RESERVES; [4] SUBBITUMINOUS

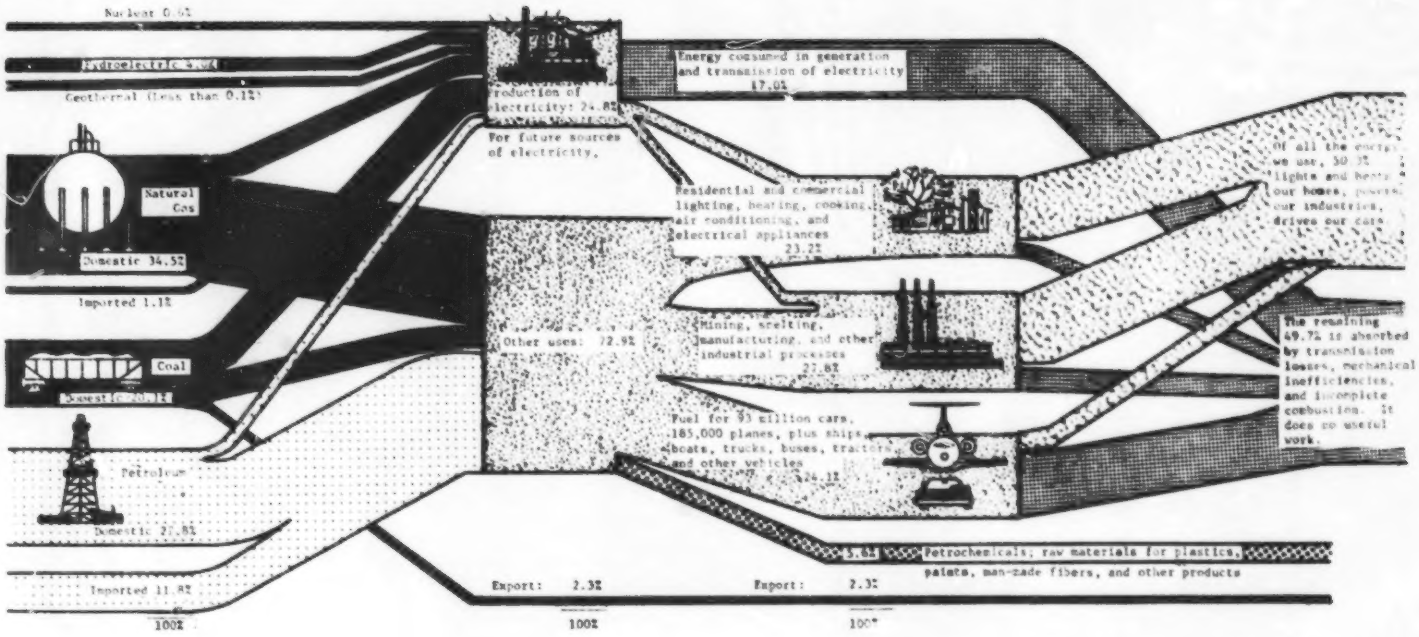

Nuclear 0.6%
Hydroelectric 4.0%
Geothermal (Less than 0.1%)
Natural Gas
Domestic 34.5%
Imported 1.1%
Coal
Domestic 20.1%
Petroleum
Domestic 27.8%
Imported 11.8%
100%
Production of electricity: 24.8%
For future sources of electricity.
Other uses: 72.9%
Energy consumed in generation and transmission of electricity 17.0%
Residential and commercial lighting, heating, cooking, air conditioning, and electrical appliances 23.2%
Mining, smelting, manufacturing, and other industrial processes 27.8%
Fuel for 93 million cars, 185,000 planes, plus ships, boats, trucks, buses, tractors, and other vehicles 24.1%
5.6%
Petrochemicals; raw materials for plastics, paints, man-made fibers, and other products
Export: 2.3%
100%
Export: 2.3%
100%
Of all the energy we use, 50.3% lights and heats our homes, powers our industries, drives our cars.
The remaining 49.7% is absorbed by transmission losses, mechanical inefficiencies, and incomplete combustion. It does no useful work.

Fig. 3-1. Energy consumption and usage in the United States (1971).

Not all of the low-sulfur recoverable reserves shown in Table 3-1 are readily available for use. Factors affecting availability are 1) location with respect to the market, 2) allocations for noncombustion use, such as for production of metallurgical coke, 3) state of development of mining and transportation facilities, and 4) Federal and other restraints on resource development. These factors, especially location and allocations for noncombustion use, have significant effects upon costs. Although the capability is potentially available for mining and transporting low-sulfur coal to the consumer, the extent to which this capability will be developed and utilized largely depends on air pollution control requirements and on the costs and technological statuses of gas cleaning, fuel desulfurization, coal gasification, and fuel substitution.

3.1.2 Oil

Fuel oils are classified into two main categories—distillates and residuals. Distillates are subclassified primarily into Grades 1 and 2. These two grades are used in certain industrial processes, where the maximum firing rate is 21 to 26 (10^6) m^3/s, and in home and apartment heating and hot water systems. Some heavy distillates, along with residuals, are subclassified into three commercial grades: Grades 4, 5, and 6. Grades 4 and 5 are primarily used for heating commercial and industrial buildings, and Grade 6 for firing large boilers in public utility, industrial, and commercial installations and in large diesel engines. Marine users often classify Grade 6 as "bunker fuel oil" or "Bunker C." The average sulfur content of Grades 4, 5, and 6 ranges from 0.5 to 5 percent, with average values of 0.75 to 2.5 percent.

Fuel cells are electrochemical devices that produce electricity through direct conversion of chemical energy. They differ from batteries in two major respects: they operate continuously as long as fuel and oxidizer are supplied from an external source, and the electrolyte remains chemically unchanged—that is, it need not be recharged. Application of fuel cells has to date been limited to uses such as space research because of the high initial cost. Providing energy to transportation vehicles is a possible application. Widespread application will, however, depend on technological advances sufficient to reduce initial cost and permit the use of low-cost fuels. Some experts feel that sufficient information is already available to design a large-scale power plant using a high-temperature cell with coal as a fuel.

Incineration of refuse produces heat that is usually wasted. This heat might be used to produce steam, which would have many applications. Several cities are now using this fuel to supply part of the heat to their municipal buildings and to provide a limited quantity of electric power. In Germany, the heating value of mixed refuse averages up to 0.1 MJ/kg; this value is expected to increase because the trend is toward less garbage and more paper and plastics. The sulfur content of refuse normally averages 0.2 to 0.7 percent.

Current estimates of United States proven crude oil reserves are in the range of 5.9 (10^9) m^3. The world's known recoverable petroleum reserves are distributed approximately 16 percent in the United States, 65 percent in the Middle East, 6 percent in Venezuela, and 10 percent in Asian and Eastern European countries as shown in Table 3-2.[2] Table 3-3[3] contains the distribution of crude oil production by sulfur content. In mid-1972, the United States crude production of 1.5 (10^6) m^3 per day and the imported crude of 0.3 (10^6) m^3 per day totaled 670 (10^6) m^3 per year.[2] The demand for petroleum products in excess of domestic production has caused an increasing reliance on imported crude. In the six years from 1966 to 1972, the United States consumption of imported crude rose from 150 (10^6) to 270 (10^6) m^3 per year.

The world 1970 refinery yields by types of fuel are shown in Table 3-4. Most of the residual fuel oil of less than 1 percent sulfur content comes from refineries that process low-sulfur crude, but much low-sulfur residual oil is obtained by desulfurization (see Section 3.3.2).

Factors affecting the availability of additional low-sulfur residual fuel oil are 1) Federal policy on low-sulfur crude and/or fuel oil production and imports, 2) state of development of production and transportation facilities, and 3) location of fuel sources with respect to consumers.

Although technology is available for refining and transporting low-sulfur fuel to the consumer, the extent to which this technology is utilized will depend largely on air pollution control requirements, the comparative costs of other control alternatives, and the Federal production and import policies.

Table 3-2. WORLD OIL RESERVES AND PRODUCTION - 1970[2]

Locations	Reserves, 10^9 m^3	Production 10^6 m^3/day	Change from 1969, percent
Asian Pacific	2.3	0.2	31.7
Europe	0.6	0.06	(-6.7)
Middle East	55	2.2	12.3
Africa	11.9	0.95	36.5
South America	3.6	0.75	2.6
North America	8.1	1.78	4.8
Other reported reserves	15.9	7.15	16.7

Table 3-3. SULFUR DISTRIBUTION OF CRUDE OILS BASED ON ANALYSES OF OILS PRODUCED IN 1966[3]

Origin of Reserves	Sulfur, weight percent						Average sulfur content, percent
	0–0.25	0.25–0.50	0.51–1.00	1.01–2.00	>2.00	Total	
United States	40.4	25.4	13.1	13.0	8.1	100.0	0.67
Canada	35.1	5.8	33.7	12.7	12.7	100.0	0.85
South America	1.6	1.3	3.5	15.2	78.4	100.0	2.26
Africa	63.7	14.4	21.6	—	0.3	100.0	0.32
Middle East	—	—	—	44.8	55.2	100.0	2.13
	Crude oil production, 10^6 m^3						
United States	0.54	0.34	0.17	0.17	0.11	1.33	—
Canada	0.05	0.01	0.05	0.02	0.02	0.15	—
South America	0.01	0.01	0.02	0.10	0.51	0.65	—
Africa	0.28	0.06	0.09	—	0.001	0.43	—
Middle East	—	—	—	0.66	0.81	1.47	—

Table 3-4. DISTRIBUTION OF REFINERY YIELD [3]

	Total output, 10^9 m^3	Gasoline and jet fuel, percent	Distillate fuel, percent	Residual fuel, percent	Other products, percent
United States	664	57.5	21.4	6.2	14.9
Other North America	97	38.3	25.9	19.5	16.3
Central America and Caribbean	38	22.8	13.0	46.4	17.8
South America	221	20.3	14.5	53.3	11.9
Western Europe	679	16.7	30.5	37.1	15.7
Middle East	134	19.1	19.7	47.8	13.4
Africa	32	27.9	26.4	33.8	11.9
Asiatic Area	308	17.8	15.3	41.8	25.1

3.1.3 Natural Gas

Natural gas is a mixture of low molecular weight hydrocarbons, with methane the major constituent. Sulfur in natural gas is mainly H_2S and is usually reduced to less than 0.1 percent before transmission (see Section 3.3.3). Natural gas occurs primarily in three ways: dissolved in crude oil, in gas reservoirs above crude oil, or in separate gasfields.

Linden[4] projects that by 1980 proven United States reserves (48 states) will be 5.4 (10^{12}) m^3 (at 101.3 kN/m^2 288K)—a net reduction from 8.1 (10^{12}) m^3 in the peak year, 1967-68.

The 1970 United States consumption of natural gas was 0.62 (10^{12}) m^3. Interstate transportation of this fuel is controlled by regulatory agencies such as the Federal Power Commission. To meet growing demand, several producers have begun development of liquified natural gas (LNG) processing, and several terminals and cryogenic tankers are in operation transporting LNG from African fields. A major contract has also been completed with the Soviet Union. Imported LNG is currently more expensive than domestic natural gas.

Natural gas liquids are byproducts of natural gas production; the ratio of natural gas to natural gas liquids is approximately 5.3 (10^3) m^3/m^3. Total proven United States reserves are estimated to be about 1.4 (10^9) m^3. The 1968 net production of natural-gas liquids[5] was approximately 87 (10^6) m^3: liquid-petroleum gases and methane accounted for 61 percent; natural gasoline and isopentane, 29 percent; other products, 8 percent; and finished gasoline and naphtha, 3 percent.[6] The sulfur content of these fuels is usually less than 0.1 percent.

Factors affecting the availability of additional natural gas and natural-gas liquids are 1) the availability of proven reserves, 2) Federal domestic and foreign fuel-use policies, and 3) the state of development of production and transport facilities.

Although technology is available for producing and transporting natural gas to the consumer, the extent to which this technology is utilized will largely depend upon Federal fuel policies.

3.1.4 Synthetic Gas

Because of the shortages of natural gas, there has been renewed interest in synthetic gases.[2] The National Petroleum Council estimates that 63 Gkg per year of coal will be converted into gas and oil by 1985.[7] Information on coal and oil gasification is given in Section 3.3.

3.1.5 Synthetic Crude

Synthetic crude made from oil shale, tar sands, and coal are potential substitutes for domestic crude oil. Oil shale formations in the western United States occupy about 41.5 (10^9) m^2 and are estimated to contain 95.5 (10^9) m^3 of crude oil in deposits assaying more than 104 cm^3 per kg of shale.[6]

The Athabasca tar sands were tapped in 1967 with a commercial plant to upgrade the crude, which is then piped to refineries.[8] Information on coal liquefaction is given in Section 3.3. The cost of these fuels is not currently competitive with coal, petroleum fuels, or natural gas.

3.1.6 Hydroelectric Power

Hydroelectric power, which only contributes about 4 percent of United States energy, is expected to increase in quantity but to reduce in national percentage. Hydroelectric plants are not sources of air pollution.

3.1.7 Nuclear Power in the United States

By the end of 1972, about 150 nuclear generating units totaling approximately 130 million kilowatts were on order, under construction, or operable.[9] The utility industry has committed over $45 billion to nuclear plant capital investment (including initial fuel), and lifetime power costs from nuclear plants now committed will approach $225 billion. Approximately 3 percent of the present electrical generating capability is nuclear, but the Federal Power Commission estimates that about 21 percent will be nuclear in 1980 and 38 percent in 1990.[10] About 65 of the units presently committed exceed 1 million kilowatts each of electric generating capacity.

Although present day power reactors utilize only a small fraction of the available nuclear raw material, some concern has been expressed about whether a sufficient amount of material to meet projected requirements can be obtained. However, known reserves and potentials at economically usable costs (up to $7 per kg of U_3O_8) will meet projected requirements to the late 1990's.[11]

Intensive development and demonstration of fast breeder reactors (which create more fissionable material than they consume) is being undertaken by the Atomic Energy Commission and by private industry. If these reactors perform according to expectations, the energy that can be extracted from the low cost ores will be extended by a factor of about 50. The relative insensitivity of breeder reactors to ore prices will also make usable the large amounts of uranium available from higher cost ores. Significant commercial utilization of fast breeder reactors for power generation is expected in the late 1980's.

Since nuclear power does not involve combustion, there is no release to the environment of sulfur oxides or other combustion products. There are other aesthetic, environmental benefits—for example, reduced acreage requirements along with elimination of tall stacks, coal-handling and storage facilities, ash disposal facilities, and railroad switchyards.

Constant, close attention must be given, however, to the maintenance of high quality in design, construction, and operation to assure the safety and reliability of nuclear power plants.

Consideration must also be given to the problem of disposal of waste heat. Because of a lower overall thermal efficiency, current commercial nuclear plants reject more waste heat to the environment than modern fossil-fueled plants. Advanced nuclear power plants now under development will have thermal efficiencies equal to the best fossil-fueled plants.

There are no SO_2 emissions from nuclear power plants.

3.1.8 Other Energy Sources

Although it is projected that until the year 2000 the United States will continue to derive the major portion of its energy from fossil fuels supplemented by nuclear energy and hydroelectric power, several other energy sources produce little or no SO_2 emissions. Solar energy, or radiation from the sun, is an inexhaustible source of power—approximately 144 000 TJ per second, a far greater amount than that being generated from fossil fuels. Application of solar power in the United States has been very limited, due largely to technical and economic problems of conversion.

Geothermal heat reservoirs underlying the volcanic regions of the earth provide heat either as hot water or steam under pressure. In the United States, the Pacific Gas and Electric Company has operated small geothermal plants since 1959. Availability of geothermal heat is limited to the western parts of the United States.

3.2 ENERGY RESOURCE CONSERVATION

Since, for any given fuel, potential sulfur oxides emissions are directly proportional to fuel consumption, energy resource conservation is a possible means for sulfur oxide emission control. The prime techniques for energy resource conservation are curtailment of energy use and improvement of the efficiency of heat use and recovery.

3.2.1 Curtailment of Energy Use

Energy use may be curtailed by reducing the consumption of useful goods and utilities or by reducing wasteful consumption of goods and utilities. Examples of the former type of curtailment are reductions in the consumption of the various products, the production of which involves energy consumption; reductions involving discontinuing use of electrical equipment; and reductions involving curtailments of fuel use. Although the concepts involved in this type of curtailment are simply to understand with respect to the air pollution control benefits to be realized, this type of curtailment is most complex to apply because of the changes in life styles involved whenever consumers are deprived of useful goods and utilities.

The second type of energy use curtailment involves minimizing wasteful consumption of energy. Opportunities exist both industrially and domestically for this type of curtailment. This type of curtailment can be achieved by minimizing the waste of products, most of which involve the use of energy, by minimizing the unnecessary use of electrical energy and fuels and by the application of more effective insulating techniques.

3.2.2 Heat Recovery

Most modern heat recovery systems are designed to economically recover heat value—i.e., the designer limits the size and mode of the system so that the value of the heat recovered slightly exceeds the cost of recovery. By extending the size, number, and/or mode of heat recovery systems, energy resources can be further conserved beyond the point of economic return, thereby further reducing fuel consumption at a cost. Although, in general, heat is recovered up to the economic breakpoint because of the substantial, continuing savings involved, it is quite possible that more comprehensive study of processes involving thermal energy would reveal additional situations in which recovery of heat now being wasted would be economical.

Heat can also be recovered from combustible materials which are now being wasted. Although, in general, most wastes which can be burned with economic return are currently used as fuels, further comprehensive studies would probably reveal additional stituations in which materials now being wasted could be burned profitably. Energy can also be further conserved by recovering heat from combustible wastes beyond the economic breakpoint.

3.2.3 Improvement of Thermal Efficiency of Combustion Units

Because for most modern combustion units, substantially all of the combustible components of the fuel are oxidized in the combustion process, there is little margin for conservation of energy resources by improvement of combustion efficiency. There is a limited potential for improvement of the thermal efficiency of combustion units. Most modern boilers and heaters are expertly designed for efficient transfer of the heat of combustion. For example, the thermal efficiency of a modern power boiler operating at high outlet temperature and 15 percent excess air usually exceeds 85 percent. Such designs allow little margin for further improvement, as the designer is limited to maintaining outlet gas temperatures sufficiently high to minimize corrosion. Although the thermal efficiency of smaller combustion units is somewhat lower, the design thermal efficiency of other modern, expertly designed combustion units, including home heating furnaces, exceeds 75 percent. There are some units which are poorly or necessarily designed to operate at high stack temperatures and with large volumes of excess air with thermal efficiencies as low as 50 percent. The poorly designed units are the exception rather than the rule and are usually owner or operator designed. There is, therefore, only a limited margin for improvement of thermal efficiency by improvement of design.

There is more potential for improvement of thermal efficiency by improved maintenance of expertly designed combustion units. Examples of maintenance practices which contribute to reduced thermal efficiency are failures to maintain burners in proper operating conditions, failure to maintain or adjust fuel-air ratio control systems, those practices which involve fouling of heat transfer surfaces, and those practices which allow excess air to enter combustion equipment through unrepaired openings.

3.2.4 Energy Conversion Efficiency Improvement

Large quantities of energy are exhausted to the environment which serve no useful purpose. For modern, efficient, expertly designed steam-electric, fossil-fuel fired- power plants, less than 40 percent of the heat content of the fuel is converted to electrical energy. Losses of energy are also involved in the hydraulic and nuclear generation of electrical power with efficiencies ranging from 30 to 35 percent for nuclear generation and about 85 percent for hydraulic generation. Additional energy losses occur as the electrical energy is transmitted to the ultimate point of use, and there are even more significant losses involved in converting the electrical energy to other sorms, such as mechanical or light energy.

At times it may be possible to lessen some of these energy losses by heat recovery schemes discussed in Section 3.2.2. Two schemes under study for improving the conversion efficiency of electric power generation are as follows.

3.2.4.1 Magnetohydrodynamics[12] —One concept involves the use of a magnetohydrodynamic (MHD) generator as the first step in power generation of an MHD "topping plant" combined with a conventional steam "bottoming plant." Basically, MHD is a technique in which the thermal energy of a hot gas is converted first to kinetic energy and then directly to electricity by the mass interaction of an electromagnetic field with the hot, rapidly moving, electrically conductive gas.

It is possible that the thermodynamic efficiency of MHD conversion of fuel to electrical energy will ultimately reach 50 percent or even higher.

Although direct conversion of thermal energy to electrical energy by MHD is appealing, the physical problems are formidable. One must cope with gas temperatures in the range of 2750 to 3311 K and with the slagging, corrosive, and erosive effects of mineral matter in the fuel. If existing problems are overcome, the MHD system, with its higher efficiencies, promises more effective use of resources and an opportunity for better control of the effluent-gas SO_2.

The first practical application of the MHD generator is being tested at the Air Force's Arnold Engineering Development Center in Tennessee. This device, using a treated coal at present, has a maximum operating time of only 120 seconds. It also has a potential for high nitrogen oxide emissions.

3.2.4.2 Electrogasdynamics -- Electrogasdynamics (EGD), like MHD, is a direct energy conversion technique in which the kinetic energy of a flowing gas is directly converted into low-amperage, high-voltage electricity. In this process, positive ions are formed on the particles in the coal combustion gases by means of a corona discharge. These charged dust particles are carried downstream to the collector electrodes, where they build up an electrical charge, which flows through an external load. Current is forced through the load resistance as the gas does work in pushing the charged electric field in the generator.[13]

The primary advantages of an EGD coal-fired station are that it can operate at high efficiency and can be built at a low capital cost. These advantages result from the simplicity of the EGD system compared to conventional stations.

Preliminary studies, while rather speculative, indicate that EGD systems can operate at an efficiency of 45 percent or higher.[14]

There still remain many difficult engineering problems such as better ion sources, a better understanding of the mobility of charged particles, and new ways to match load impedances of the generator and the load. If all technical difficulties can be overcome, this process will have the potential of generating cheaper electricity at a smaller capital cost and with some reduction in SO_2 emissions. At present, experiments are being conducted under contract with the Office of Coal Research of the Department of the Interior. A pilot-plant EGD power station is planned for 1972 or 1973. As with the MHD technique, the EGD has a potential for high nitrogen oxide emissions.

3.2.4.3 Gas Turbine Power Generation — Although gas turbines are normally powered by low-sulfur fuels, such as pipeline natural gas or petroleum distillates, consideration has been given to the use of higher sulfur fuels as discussed in Section 3.4.1.10.

There are several options available for energy resource conservation in conjunction with the application of gas turbine power generation systems. The efficiency of conversion of the thermal energy of the gross heating value of the fuel to electrical energy is slightly less than 30 percent for efficiently designed single-cycle gas turbine systems which exhaust the gases to the atmosphere with little heat recovery.[15] Efficiency is increased to about 35 percent in regenerative gas turbine systems which incorporate heat exchange systems which preheat the combustion air.[15] In combined cycle systems, some of which convert 40 percent of the gross thermal energy of the fuel to electrical energy, heat from the exhaust gases is recovered to produce steam which is then used to generate additional electrical energy.[15] The options are also available to use the steam directly or from the steam turbine for heating and to fire additional fuel for steam production. The efficiency of this latter type of system for conversion of the gross heating value of the fuel to electrical energy and to transfer thermal energy to the steam produced can exceed 70 percent.[15]

There are numerous commercial applications of single-cycle and regenerative systems somewhat less in demand. A system producing process steam in conjunction with a gas turbine power generation system is installed at the Dow Chemical Company, Pittsburgh, California.[16] In another application the gas turbine-steam generation type of system was installed at the Buck Station of Duke Power Company in conjunction with the phaseout of two deteriorated conventional power boilers.[17] This repowering scheme involved use of the steam produced to power the original 1926-vintage steam turbine power generation system.

3.3 FUEL DESULFURIZATION

Basic fuel desulfurization technology has been available for over 20 years and has been advanced over the past decade by process improvements and by the introduction of new processes. The status of fuel desulfurization, especially of oil and gas, has risen; but desulfurization of coal is still primarily by mechanical preparation. Reductions in fuel sulfur content may adversely affect the efficiency of electrostatic precipitators for removing particulate matter from the gas stream. Reductions can be compensated by modifications which often involve the installation of additional equipment.

3.3.1 Coal Desulfurization

Sulfur in coal occurs in three forms: as a sulfate in trace quantities, as organically bound sulfur in the molecular structure, and as mineral sulfur; mostly pyrite but also marcasite. Mechanical coal preparation techniques can remove only pyritic sulfur, but liquefaction, gasification, and solvent refining can remove other forms as well.

3.3.1.1 Mechanical Coal Cleaning--Mechanical cleaning methods in use in the United States are selective mining, manual or mechanical separation of impurities, froth flotation, and gravity concentration.[18]

Mechanical strip and auger mining produce most of the coal mined in the United States. Manual cutting, in which the impurities in the coal can be reduced by selective cutting, is still performed; increasing use of mechanical devices, however, has greatly reduced this practice.

After mining, the next steps in coal processing are size reduction and classification. Size reduction is accomplished in two stages — breaking and crushing. Breaking the run-of-the-mine coal and removing rock and tramp iron are accomplished by rotary equipment (such as the Bradford Breaker), within which coal is raised and allowed to drop and break by the slow rotary motion of a large perforated drum. This process does not produce large quantities of fines.

Crushers, by mechanical action, further reduce the size of the coal. Several types of crushers are in use: double roll crushers, which produce small quantities of fines, and single roll crushers, hammer-mill crushers, and ring crushers, all of which produce large quantities of fines.[19]

Several types of screens are used for classification. In the bar screen, or grizzly, the bars allow the large lumps to traverse the screen while the small lumps fall through the openings. Revolving screens, similar to inclined rotating breakers, are used with sizes smaller than 0.076 m. In shaker screens, sloped downward from the feed end to the discharge end, the oversized coal rides to the discharge and the desired size falls through the holes in the screen. Equipment of this type is also used for dewatering washed coal. In vibrating screens, also sloped from feed to discharge, the high frequency vibration loosens the feed from the screen openings and aids in dewatering.

After size reduction and classification, other cleaning methods--that is, hand cleaning, froth flotation, and gravity concentration—can be used. Hand picking, the earliest method of cleaning coal, is still practiced, albeit now with mechanical assistance from shake tables. After the initial screening operation, oversized coals, 0.102 m and larger, are sent to the picking table where the impurities are manually removed. Picking facilities include belt and apron conveyors, shaking tables, and occasionally chain conveyers. Because hand picking can leave as much as 50 to 60 percent coal in the refuse, it is economical to crush the refuse and to reclaim the coal mechanically.

Froth flotation supplements other cleaning processes by recovering coal fines from coarse-coal cleaning. Flotation media, usually alcohols with a frothing agent, are agitated by air injection. The coal particles adhere to the bubbles, and the slate and shale sink to the bottom of the vessel to be removed as waste. This process is most effective for 48-mesh and smaller material.

Gravity concentration, based upon differences in specific gravity, is also used for removal of impurities. Specific gravities of coal and its impurities are shown in Table 3-5.

In a survey of 322 mines throughout the United States, samples were collected at both deep and surface mines which supply coal to the utility industry. The survey indicated that 30 percent of the samples, primarily those with intermediate sulfur concentrations, could be washed to 1 percent or less total sulfur and that total sulfur content could be reduced by nearly 50 percent in more than half of the samples by crushing the coal prior to removal of the heaviest impurities.[20] An example of reductions in uncontrolled emission rates which might result from coal cleaning are shown in Table 3-6.

Table 3-5. SPECIFIC GRAVITIES OF COAL AND IMPURITIES

Material	Specific gravity
Bituminous coal	1.1 - 1.4
Bone coal	1.3 - 1.7
Carbonaceous shale	1.6 - 2.2
Clay	1.8 - 2.2
Shale	2.0 - 2.6
Pyrite	4.8 - 5.2

Table 3-6. EFFECT OF COAL CLEANING ON UNCONTROLLED EMISSION RATES OF SO_2 AND FLY ASH

Coal cleaned	Uncontrolled Emissions			
	SO_2		Fly ash	
	kg/1000 kg of coal	μg/J	kg/1000 kg of coal	μg/J
Raw coal	85	3.44	264	10.7
Refined coal	23	1.01	43	2.04

The prime factors affecting the cost of coal preparation are production costs, waste disposal costs, shipping savings, and ease of grinding, handling, and maintenance. Therefore, estimates of the economic impact of coal desulfurization must be made on a case-by-case basis.

3.3.1.2 Coal Liquefaction —Technology for coal liquefaction has been available for decades. This technology usually involves hydrogenation and is designed to produce maximum amounts of motor fuel—the liquid fuel of highest value. Some gaseous products always result, very little heavy liquid fuel is produced, and the major product is a relatively high-sulfur char. The disposition of this char has been a major disadvantage of liquefaction processes.

Liquefaction of coal can be accomplished by one of the following four mechanisms: (1) gasification with oxygen and steam to produce a coal-gas, which can then be catalytically reformed to liquid fuels, (2) solvent refining with minimum hydrogenation, (3) solvent refining with pressurized hydrogenation, and (4) multistage pyrolysis.

Gasification and reforming --A commercial plant, the Sasol Plant in the Republic of South Africa, produces liquid fuels from coal using gasification followed by Fischer-Tropsch synthesis. Process economics, however, have not been favorable for the U.S. market so interest has not developed.

Solvent refining with minimum hydrogenation-- The PAMCO (Pittsburgh and Midway Coal Mining Company) solvent-refining process[21] utilizes minimum hydrogenation to produce a shiny, black solid fuel that liquefies at about 490 K and can thus be burned either as a solid or as a liquid.

In the process, Figure 3-2, finely ground coal and anthracene oil are slurried, hydrogen is added to prevent repolymerization, and the mixture is heated to 720 K to promote dissolution. The resulting liquid is then filtered to remove the mineral residue, which contains ash, pyritic sulfur, and some organic sulfur.

The filtered solution is flash evaporated to produce a light oil-recovered solvent vapor phase and a hot liquid residue that are cooled and solidified to the final product.

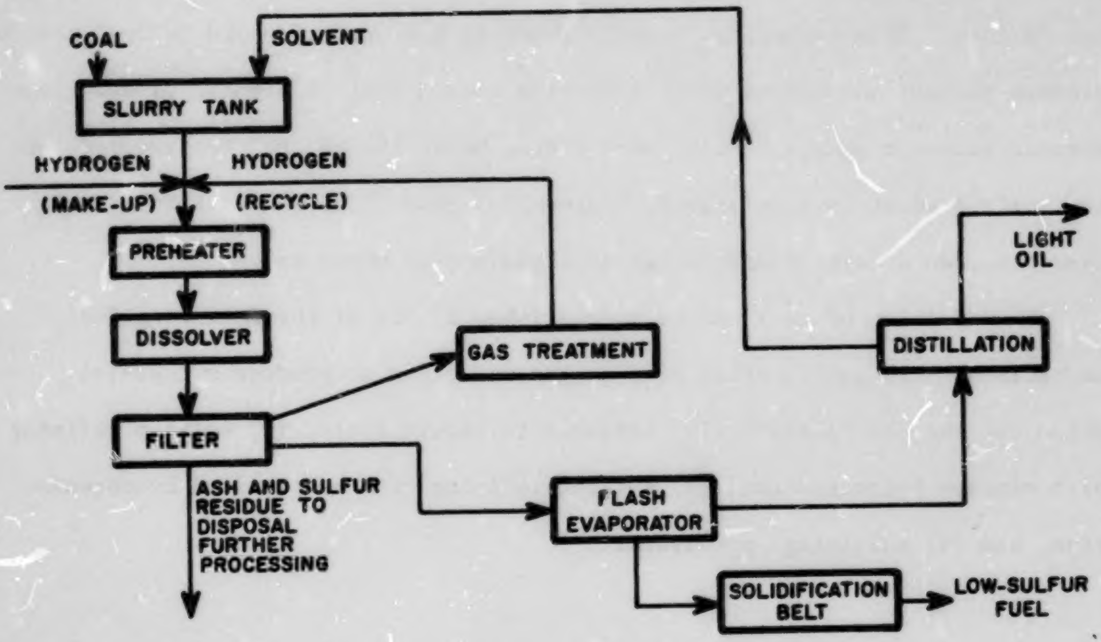

COAL
SOLVENT
SLURRY TANK
HYDROGEN
(MAKE-UP)
HYDROGEN
(RECYCLE)
PREHEATER
DISSOLVER
GAS TREATMENT
FILTER
ASH AND SULFUR
RESIDUE TO
DISPOSAL
FURTHER
PROCESSING
FLASH
EVAPORATOR
DISTILLATION
LIGHT
OIL
SOLIDIFICATION
BELT
LOW-SULFUR
FUEL

Figure 3-2. PAMCO solvent refining process.

Final product properties depend on the raw coal. Typical feed and product yields are shown in Table 3-7.

Processing costs can range from 3.8 to 18.9 cents per GJ depending on which bases are assumed for cost estimation; nonetheless, costs in this range can be attractive. The small hydrogen consumption, the advantage of no catalyst, and the emphasis on clean fuel are all desirable elements of this process.

Solvent refining with pressurized hydrogenation— An example of high-pressure hydrogenation is the Consol process,[22] originally intended to produce gasoline from coal, but subsequently converted to the manufacture of low-sulfur synthetic crude oil. In this process (Figure 3-3), coal is dissolved in a process-generated liquid, and ash and other nonreactive parts are filtered out. Solids go to a low-temperature carbonization step, which recovers solvent and produces char. The liquid stream is flashed; then the bottoms are water-washed to remove ash, catalytically hydrogenated under pressure, and refined by distillation.

Uses for the char and availability of low-cost hydrogen are major considerations in process economics. More detailed evaluation must await pilot-plant experience.

Another solvent-refining process with pressurized hydrogenation is the H-coal process (Figure 3-4). This process, developed by Hydrocarbon Research, Inc., uses hydrogenation to recover a light crude oil which can be conventionally refined to gasoline. Coal conversion rate is higher than that for other methods, as shown in Table 3-8 for Illinois #6 coal on a moisture- and ash-free basis.

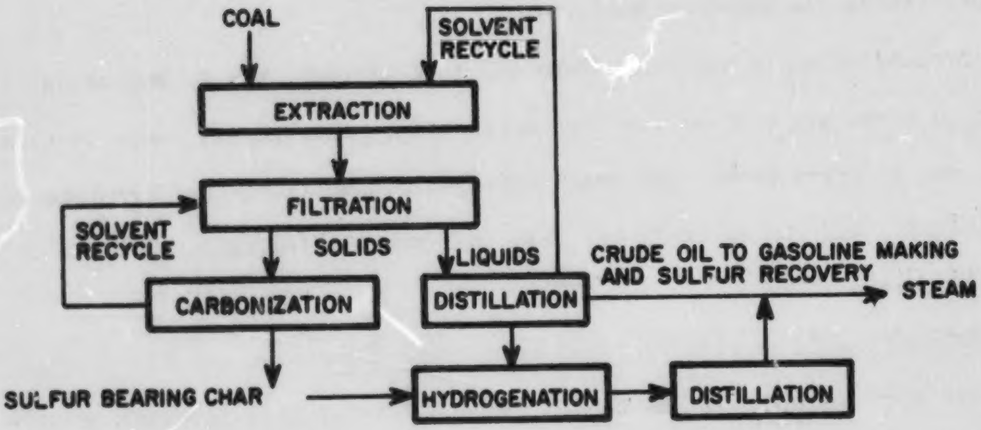

COAL
SOLVENT RECYCLE
EXTRACTION
FILTRATION
SOLVENT RECYCLE
SOLIDS
LIQUIDS
CRUDE OIL TO GASOLINE MAKING AND SULFUR RECOVERY
STEAM
CARBONIZATION
DISTILLATION
SULFUR BEARING CHAR
HYDROGENATION
DISTILLATION

Figure 3-3. Consol process (simplified flow chart).

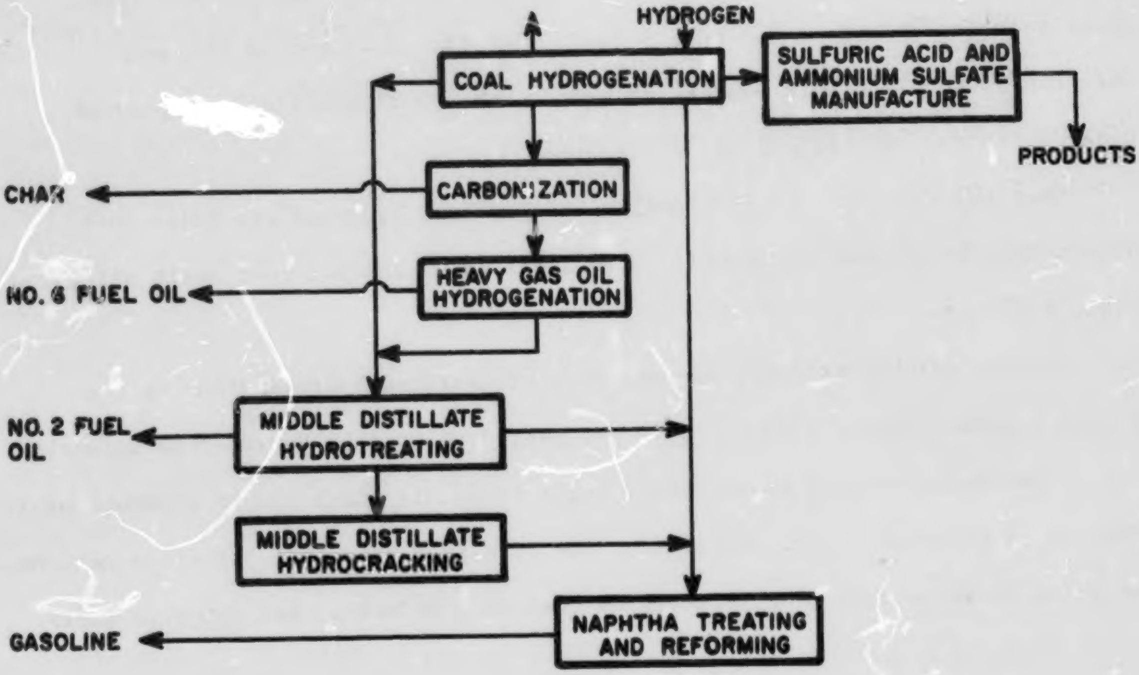

HYDROGEN
COAL HYDROGENATION
SULFURIC ACID AND AMMONIUM SULFATE MANUFACTURE
PRODUCTS
CHAR
CARBONIZATION
NO. 6 FUEL OIL
HEAVY GAS OIL HYDROGENATION
NO. 2 FUEL OIL
MIDDLE DISTILLATE HYDROTREATING
MIDDLE DISTILLATE HYDROCRACKING
GASOLINE
NAPHTHA TREATING AND REFORMING

Figure 3-4. H-Coal process (simplified flow chart).

Table 3-7. SOLVENT-REFINED COAL PRODUCT

Feed	Product yield Ash wt. percent	 Sulfur wt. percent	 Heat content MJ/kg
Raw coal (Kentucky #11)	6.91	3.27	32.5
Refined product	0.14	0.95	37.1

Coal is dried, pulverized, slurried with coal-derived oil, and charged continuously with hydrogen to a reactor containing a bed of ebullating catalyst (fluidized bed where the liquid is the fluidizing medium). The coal is hydrogenated and converted to gaseous and liquid products: refinery gases, naptha, middle distillate, and heavy gas-oil. The unconverted coal residue and the heavy liquid products are sent to the carbonization section. Recovered heavy gas-oil is catalytically hydrocracked to middle distillate, naptha, and refinery gas. The naptha is further treated and reformed to gasoline.

Ammonia and a portion of the hydrogen sulfide from the coal and heavy gas-oil hydrogenation steps are recovered as an aqueous solution of ammonium sulfide. This solution, together with the H_2S recovered from the refinery gases, is treated to convert the ammonium sulfides into ammonia and H_2S. The H_2S may be further processed to sulfuric acid; the ammonia is converted with a portion of the sulfuric acid to ammonium sulfate.

Table 3-8. PRODUCT YIELD FOR H-COAL PROCESS (Illinois #6 coal)

Product	Percent of original coal by weight[a]
Light gas	10.2
Liquid	71.0
Char	10.7
H_2S, NH_3, H_2O	8.1

[a] Moisture- and ash-free basis.

Although this process does produce low-sulfur products, the economics of the process are very sensitive to the price of light fuel oil and gasoline.

Multistage pyrolysis —FMC Corporation's Project COED (char-oil-energy development), the Office of Coal Research's oldest coal-liquefaction project, began work in May 1962.[23] This process, an example of multistage pyrolysis, produces a liquid, some gas, and char, as shown in Table 3-9.

In the COED process (Figure 3-5), crushed coal is heated to progressively higher temperatures in a series of four fluidized-bed reactors. From 1 to 5 percent of the charge is volatilized in the first stage, and 50 percent of the oil yield is derived from the second stage. Burning a portion of the char with oxygen in the last stage supplies process heat. All the volatile products from the coal produced by the last three stages exit from the second stage to the product recovery system. The gas, containing 40 to 50 percent hydrogen, can be processed further to produce methane or hydrogen. Oil processing yields conventional gasoline and fuel oil products.

Pilot plant studies are continuing; economic analyses and further evaluation will undoubtedly soon be updated based on more recent experimental results. Coal desulfurization by liquefaction can be a long-term approach to providing low-sulfur fuels if the char disposition problem can be economically managed.

Table 3-9. TYPICAL PRODUCT YIELDS FOR COED PROCESS

	Product yields			
	Char, percent	Oil, percent	Gas*	
			m^3/kg	percent
Pilot plant	56	18.7	0.28	16.9
Bench scale	60	20	0.25	15

* Gas-heat value of $19.9 MJ/m^3$ at 289 K and $101 kN/m^2$.

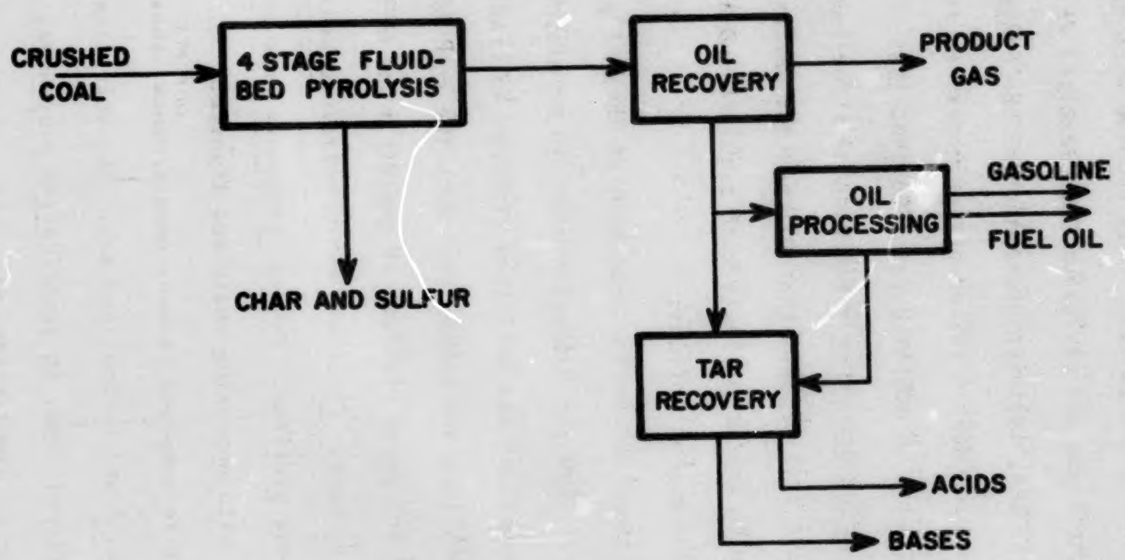

CRUSHED COAL
4 STAGE FLUID-BED PYROLYSIS
CHAR AND SULFUR
OIL RECOVERY
PRODUCT GAS
OIL PROCESSING
GASOLINE
FUEL OIL
TAR RECOVERY
ACIDS
BASES

Figure 3-5. COED process (simplified flow chart).

3.3.1.3 Gasification —Destructive distillation coal gasifiers have been operated since the early nineteenth century. During the latter part of the century, water-gas and producer-gas processes were commercially developed. With the exception of coke ovens in steelmaking, these plants have gradually disappeared in the United States as development of natural gas resources has expanded. However, increased demand for gaseous fuels coupled with projected shortages of both domestic natural gas and petroleum have resulted in renewed interest in coal gasification. Thus, improved processes for the conversion of coal to gaseous or liquid fuels are under development. However, it is unlikely that any commercial development will be achieved prior to 1980-1985.

Pipeline-quality, gas-producing processes — New processes for coal gasification mostly produce a gaseous fuel of less than 0.1 percent sulfur content. These processes also produce solid wastes or fuels with high ash and sulfur contents. The gasification steps are as follows:

1. Pretreatment - Pretreatment is usually some form of thermal processing in the presence of air. This air oxidation destroys or minimizes the caking and swelling properties and minimizes problems in handling and gasifying the coal. Swelling and caking can cause the coal particles to expand, agglomerate and cause problems if gasification is from fluid, moving, or static beds. Processes using entrained beds are less susceptible to these problems. Several processes have been developed for use only with noncaking coals and lignite.
2. Devolatilization - Coal is composed of many constituents; these can be classed as volatiles, fixed carbon, and ash. The volatiles are the hydrogen-rich fractions; thus, in gasification processes, the first step is an attempt to devolatilize the coal. As the volatiles

are driven off at temperatures in the range of 811 to 1 088 K, the methane, hydrogen, tars, and carbon residue (char) are formed. The devolatilization can be conducted in a separate vessel, in the gasifier proper, or in a top section of the gasifier.

3. Gasification - Gasification of the carbon residue is accomplished by heating the carbon in the presence of steam, air, or oxygen to produce a mixture of gases—CO, CO_2, H_2, H_2O, H_2S, and methane.
4. Gas purification - CO_2, H_2S, H_2O, and tars are removed by conventional processes; however, hot-gas cleaning is being developed.
5. Catalytic shift conversion - Part of the gas stream is converted to a hydrogen-rich fraction by the classic water-gas shift reaction, which catalytically converts carbon monoxide and water to hydrogen and carbon dioxide.
6. Methanation - The remainder of the gas, together with the hydrogen-rich fraction are catalytically reacted to produce a methane-rich gas. Carbon monoxide and hydrogen react to form methane and water.

Several processes designed to overcome problems associated with gasification are shown in Figures 3-6 through 3-10. None of these processes are cost competitive with natural gas at this time.

Low-heat content, gas-producing processes - Historically, low-heat content gas producers were known and used before natural gas became available. Producer gas was made by blowing steam and air through coke. Anthracite and some subbituminous coals were also used in fixed-bed systems.

All of the gasification processes now under development or commercially available can be modified to produce low-heat content gas (4.6 to 9.3 MJ/m^3). For utility and large-scale industrial applications, low-heat content gas has distinct advantages over high-heat content gas: (1) increase in thermal efficiency from 65 to 80 percent; (2) a simpler gasification process utilizing air instead of oxygen; (3) a simpler purification step; (4) elimination of shift, conversion, and methanation steps; and (5) reduced capital and operating costs.

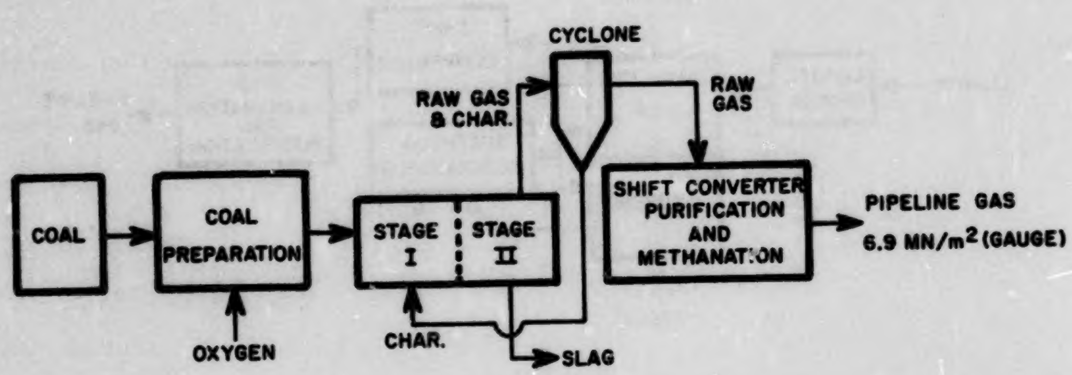
Another process improvement now under development, a hot-gas purification system to remove H_2S prior to combustion, could increase overall thermal efficiency about 90 percent.[26]

The various gasification processes which can be modified to produce low-heat content gas include the Hygas, Synthane, Bigas, and CO_2 Acceptor processes. In addition, the Lurgi, Koppers-Totzeh, Winkler, Wellman-Galusha, and other commercially available processes can be used.

The Lurgi process, using a single fixed bed and noncoking coals, can produce a low-heat content gas under pressure containing 25 percent H_2, 16 percent CO, 5 percent CH_4, and 54 percent either N_2 or CO_2.[32] A large scale (7.1 (10^6) m^3 per day) Lurgi synthetic natural gas plant is currently under design.

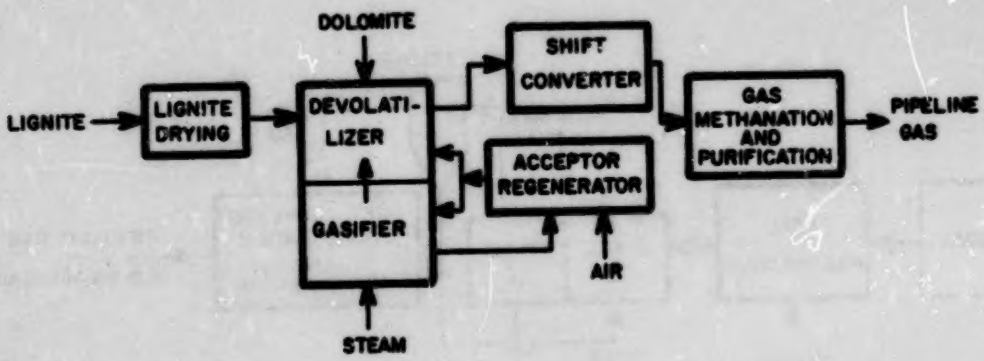
The use of fluidized, entrained, or fixed-bed, low-heat content gasifiers, coupled with gas turbines, will significantly improve the efficiency of electric generating plants. The current interest in these systems is high, and significant private and public funds are being expended to bring this technology into rapid use. The development of improved, high-temperature, gas cleaning equipment and high-pressure gas turbines, together with the development of improved gasification systems could lead to widespread use of this technology by the early 1980's.

Figure 3-6. Bigas Process, Bituminous Coal Research, Inc.[24,25,26]


CYCLONE
RAW GAS & CHAR.
RAW GAS
COAL
COAL PREPARATION
STAGE I
STAGE II
SHIFT CONVERTER PURIFICATION AND METHANATION
PIPELINE GAS
6.9 MN/m² (GAUGE)
OXYGEN
CHAR.
SLAG

PROCESS DESCRIPTION	Pulverized coal is fed to the bottom of Stage II and carried upward with a stream of hot synthesis gas produced in Stage I. The fine coal is devolatilized; volatile matter reacts with steam and synthesis gas to form a methane-rich stream; the char is separated from the gas stream, returned to Stage I, and reacted with oxygen and steam at high temperatures to produce synthesis gas which is subsequently purified and upgraded to high heat content gas; the ash is removed as slag. The gasifier operates at 6.9 to 10.3 MN/m^2 at 1 922 K exit gas temperature is 1 200 K.
PROCESS STATUS	Construction of a large-scale pilot plant incorporating all process steps at Homer City, Pennsylvania, is to be completed in early 1974. A 2- to 3-year development and test program will be conducted.
PROCESS ECONOMICS	Overall feed efficiency is 58 percent. The estimated selling price of high-heat content gas is 76¢ to 94¢ per GJ, including fuel and byproduct credit.

Figure 3-7. CO_2 Acceptor Process, Consolidation Coal Company.[25-28]

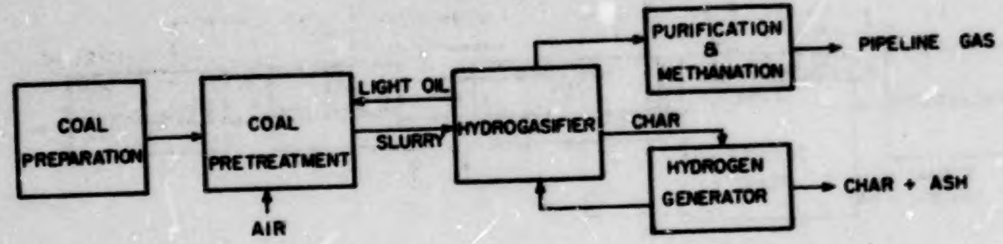

DOLOMITE
LIGNITE
LIGNITE DRYING
DEVOLATI-LIZER
GASIFIER
SHIFT CONVERTER
ACCEPTOR REGENERATOR
GAS METHANATION AND PURIFICATION
PIPELINE GAS
AIR
STEAM

PROCESS DESCRIPTION Crushed lignite (or possibly noncaking coal) is dried, heated, and fed to the devolatilizer, where it is mixed with calcined dolomite at 1 100 K and 931 kN/m^2. The char-dolomite is gravity fed to the gasifier, where steam and additional calcined dolomite are added. Gas from the gasifier passes through the devolatilizer and, together with the devolatilizer offgas, is sent to the shift converter and through gas purification and methanation steps; residual char and spent dolomite are sent to the regenerator, where the dolomite is regenerated and the residual char is used as fuel. The dolomite acts as a heat carrier (it leaves the regenerator at 1 290 K) and as the acceptor—that is, it removes CO_2 and H_2S from the gas stream.

PROCESS STATUS A 27,000 kg-per-day pilot unit being operated in Rapid City, South Dakota, will produce design information for full-scale plants. A 2- to 3-year test program is planned.

PROCESS ECONOMICS Pipeline gas will sell for 34¢ to 55¢ per GJ, plus the cost of lignite.

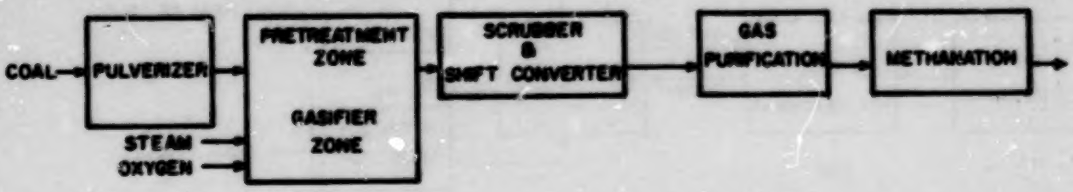
Figure 3-8. Hygas Process, Institute of Gas Technology.[25,26]


COAL PREPARATION
COAL PRETREATMENT
AIR
LIGHT OIL
SLURRY
HYDROGASIFIER
PURIFICATION & METHANATION
PIPELINE GAS
CHAR
HYDROGEN GENERATOR
CHAR + ASH

PROCESS DESCRIPTION Dried coal is pulverized, pretreated (if necessary) with air at 670 K to make it noncaking, and slurried with a light oil from the process. The slurry is pumped to a fluidized-bed hydrogasifier operating at 10.3 MN/m^2 (gauge) The first stage of the gasifier, operating at 588 K, is where the light oil flashes off (it is subsequently recovered for reuse). The coal passes to the next stage, operating at 970 to 1 080 K, where it reacts with a hydrogen-rich gas and steam to produce a product gas rich in methane. The final stage, operating at 1 200 to 1 2[illegible] K, reacts steam and hydrogen with the partially converted coal to form a methane-rich gas and a char. The char is sent to another vessel, where it reacts with steam to produce CO, H_2, and unreacted char; the CO and H_2 gases are used in the hydrogasifier; the total product gas is purified and methanated. The hydrogen generation step may be either electrothermal, steam-iron, or steam-oxygen.

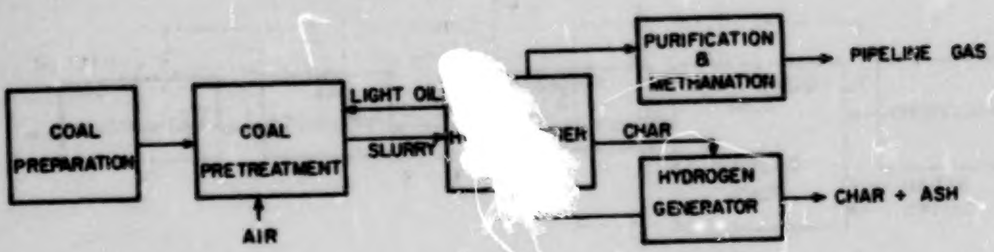
PROCESS STATUS A 72,560 kg-per-day Hygas pilot plant has been constructed The test program will be completed in 2 or 3 years.

Figure 3-9. Synthane Process, U.S. Bureau of Mines.[25,26,29]


COAL
PULVERIZER
STEAM
OXYGEN
PRETREATMENT ZONE
GASIFIER ZONE
SCRUBBER & SHIFT CONVERTER
GAS PURIFICATION
METHANATION

PROCESS DESCRIPTION	Coal is pulverized to 70 percent through 200-mesh with a 35-mesh top size and fed to the pretreatment zone of the gasifier, where contact with steam and a small quantity of oxygen at 670 K and 4.1 MN/m^2 causes partial devolatilization. The pretreated coal drops to the gasification zone, where the reaction with steam and oxygen is completed at 1 200 K and 4.1 MN/m^2; the product gas is scrubbed to remove tars and then passed through a shift converter; the hydrogen-CO-rich stream is purified and passed through a methanator of special design to produce pipeline gas.
PROCESS STATUS	A 2,700 kg-per-hour pilot plant is under design. Construction is proposed to start before mid 1974.
PROCESS ECONOMICS	The gas selling price, exclusive of fuel, is 42¢ to 72¢ per GJ, depending on 20-year or 5-year amortization respectively.

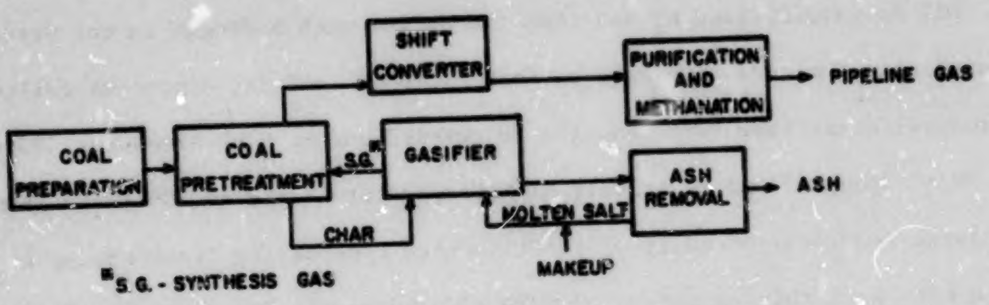
Figure 3-8. Hygas Process, Institute of Gas Technology.[25,26]


COAL PREPARATION
COAL PRETREATMENT
AIR
LIGHT OIL
SLURRY
CHAR
PURIFICATION & METHANATION
PIPELINE GAS
HYDROGEN GENERATOR
CHAR + ASH

PROCESS DESCRIPTION Dried coal is pulverized, pretreated (if necessary) with air at 670 K to make it noncaking, and slurried with a light oil from the process. The slurry is pumped to a fluidized-bed hydrogasifier operating at 10.3 MN/m^2 (gauge). The first stage of the gasifier, operating at 588 K, is where the light oil flashes off (it is subsequently recovered for reuse). The coal passes to the next stage, operating at 970 to 1 080 K, where it reacts with a hydrogen-rich gas and steam to produce a product gas rich in methane. The final stage, operating at 1 200 to 1 255 K, reacts steam and hydrogen with the partially converted coal to form a methane-rich gas and a char. The char is sent to another vessel, where it reacts with steam to produce CO, H_2, and unreacted char; the CO and H_2 gases are used in the hydrogasifier; the total product gas is purified and methanated. The hydrogen generation step may be either electrothermal, steam-iron, or steam-oxygen.

PROCESS STATUS A 72,560 kg-per-day Hygas pilot plant has been constructed. The test program will be completed in 2 or 3 years.

Figure 3-10. Molten Carbonate Process, M. W. Kellogg Company.[25,26,30,31]


SHIFT CONVERTER
PURIFICATION AND METHANATION
PIPELINE GAS
COAL PREPARATION
COAL PRETREATMENT
S.G.*
GASIFIER
ASH REMOVAL
ASH
MOLTEN SALT
CHAR
MAKEUP
*S.G. - SYNTHESIS GAS

PROCESS DESCRIPTION	Coal is ground to 12-mesh, dried, and pretreated with synthesis gas and steam at 1 080 K and 8.3 MN/m^2 to partially hydrogenate the coal and to yield some methane and hydrogen. The hot char from the preheater goes to the gasifier, which consists of a molten carbonate bath operating at 1 220 K and 8.3 MN/m^2. The synthesis gas from the gasifier is used in the pretreater; the gas from the pretreater goes through heat recovery, water-gas shift, purification, methanation, and drying to produce pipeline gas.
PROCESS STATUS	Based on bench-scale tests and extensive engineering design and evaluation, M. W. Kellogg is proceeding with plans to design, construct, and operate a pilot plant. Intermediate-scale tests are underway to test significant process variables over the next 3 to 5 years.
PROCESS ECONOMICS	The estimated selling price of pipeline gas is 60¢ to 85¢ per GJ.

3.3.2 Oil Desulfurization

Oil is desulfurized by reacting the sulfur with hydrogen in the presence of specially designed catalysts to form hydrogen sulfide, a process called hydrodesulfurization. The reaction is carried out at high pressures (30 to 140 MN/m^2 [gauge]) and relatively high temperatures (610 to 700 K) in large catalytic reactors—normally of the fixed-bed type having diameters up to 4.3 m with wall thicknesses up to 0.20 m. The resulting hydrogen sulfide gas is subsequently removed and treated by methods discussed in Section 3.3.3.

Hydrodesulfurization can be applied directly to atmospheric resid, as shown in Figure 3-11 D, or the resid can be subjected to vacuum distillation first. Several processes in which the products of vacuum distillation are desulfurized are shown in Figures 3-11, A, B, and C.

The first process involves vacuum distillation, hydrodesulfurization of the vacuum gas oil, and then blending of the treated oil with the vacuum bottoms.

In the second process the vacuum bottoms are further processed to remove asphalt fractions. The de-asphalted fraction and the vacuum gas oil are desulfurized and mixed with the asphalt fraction to produce a lower sulfur fuel oil.

In the third process, vacuum distillation is followed by vacuum gas oil, the de-asphalted fraction, and the asphalt fraction. The asphalt fraction is coked; the coker gas oil is hydrodesulfurized and blended with desulfurized vacuum gas oil and de-asphaltized oil to form a low sulfur fuel oil.

In hydrodesulfurization of atmospheric resid, sulfur levels can be reduced to 0.3 to 1.0 weight percent. In vacuum gas oil hydrodesulfurization, Figure 3-11-A, sulfur reductions down to 1.0 to 2.5 weight percent sulfur,

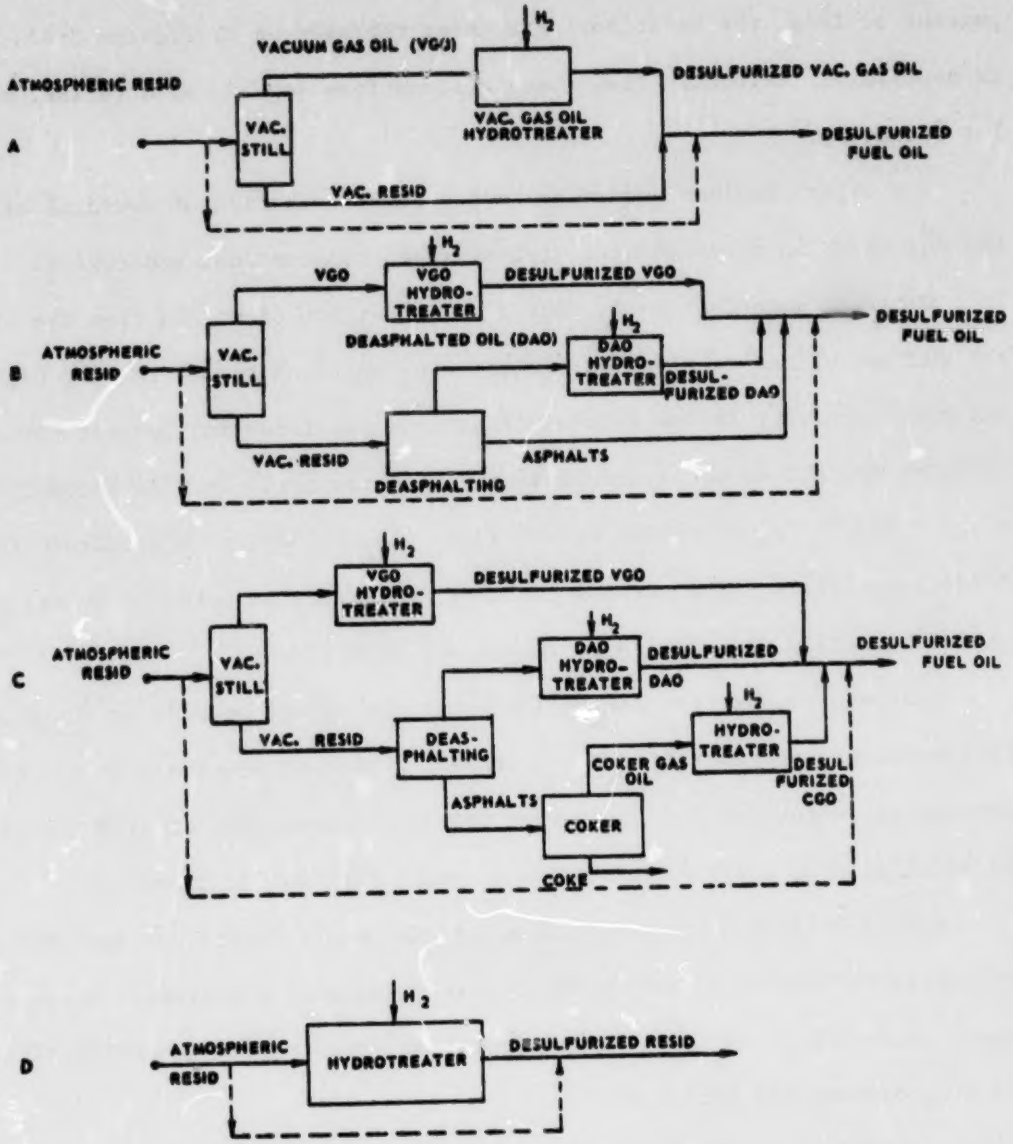

A
ATMOSPHERIC RESID
VACUUM GAS OIL (VGO)
H_2
VAC. STILL
VAC. GAS OIL HYDROTREATER
DESULFURIZED VAC. GAS OIL
DESULFURIZED FUEL OIL
VAC. RESID
B
ATMOSPHERIC RESID
VAC. STILL
VGO
H_2
VGO HYDRO-TREATER
DESULFURIZED VGO
DEASPHALTED OIL (DAO)
DAO HYDRO-TREATER
DESUL-FURIZED DAO
DESULFURIZED FUEL OIL
VAC. RESID
DEASPHALTING
ASPHALTS
C
ATMOSPHERIC RESID
VAC. STILL
VGO HYDRO-TREATER
DESULFURIZED VGO
DAO HYDRO-TREATER
DESULFURIZED DAO
DESULFURIZED FUEL OIL
VAC. RESID
DEAS-PHALTING
HYDRO-TREATER
COKER GAS OIL
DESULFURIZED CGO
ASPHALTS
COKER
COKE
D
ATMOSPHERIC RESID
HYDROTREATER
DESULFURIZED RESID

Fig. 3-11. Hydrodesulfurization processes

depending on the crude, are realizable. For many crudes to get to 0.3 weight percent or less, the additional treatment represented by Figures 3-11, B or C is necessary. Selection from these alternatives depends on a refiner's particular situation.

The major problems occurring in the desulfurization of residual oil are the deactivation of catalysts, high hydrogen consumption, and coking.

Catalyst deactivation is caused by deposition of metals from the oil on the surface of the catalyst particles. One approach to maintaining high catalytic activity is the removal of ash and metal-forming constituents before charging the oil to the hydrodesulfurization reactor. This is accomplished in several ways: by preheating the resid to 640 to 750 K to agglomerate the ash-forming materials, by absorbing the tarry materials on coke, or by using bauxite, ceramics, metals, or alumina to remove ash constituents.

Hydrogen consumption exerts a significant effect on process costs because of the expense of generating the hydrogen. Hydrogen requirements increase with increasing sulfur content, but since hydrogen reacts with other molecules, more is required than would be necessary to react with sulfur alone.

Coking becomes a problem because of the severe conditions required for the hydrodesulfurization of resids to achieve a low sulfur content. These conditions cause coking of high boiling fractions, thus reducing catalyst life and causing operational problems.

Atmospheric residual hydrodesulfurization is not as widely applied as the vacuum gas oil process.[32,33] Only 20.7 (10^3) m^3/D is currently in operation, and all of this is in Japan. Research on this process is directed at being able to process the higher sulfur and higher metals crudes and at achieving substantial cost reductions.

Vacuum gas oil hydrodesulfurization has shown a strong growth since 1967 as shown in Figure 3-12.[33] It has been the most economical first step in obtaining the desulfurization levels needed thus far. Caribbean installations have served as the primary facilities for making low sulfur fuel oil for the U.S. market. Vacuum gas oil hydrodesulfurization is a well-developed technology. There are seven major oil companies who have developed processes which are available for license.

De-asphalting and coking are well established technologies; however, the suitable disposal of the high sulfur asphalt or high sulfur coke is a key problem area.

In order to minimize the problem of high sulfur coke disposal, a new process has been developed which cokes the vacuum resid and also gasifies the coke. The products from this process, called FLEXICOKING, are a vacuum gas oil which can be desulfurized and a low sulfur, low heat content gas which can be burned in or near the refinery. A schematic diagram of the process scheme is shown in Figure 3-13. The first commercial unit is now being designed for a refinery in Japan.

The BRD is supplied with crude oils mainly from north Africa and Nigeria. Since these oils have very low sulfur contents no desulfurization has been used until now.

Only distillate oils are desulfurized in the BRD. The processes used are hydrotreating and hydrofining; they are primarily applied to fuel oils from cracking-units because of their high sulfur content.[34]

3.3.3 Gas Desulfurization

The major gaseous sources from which sulfur must be removed are natural gases, petroleum refinery gases, and sulfur plant tail gases. A sulfur plant

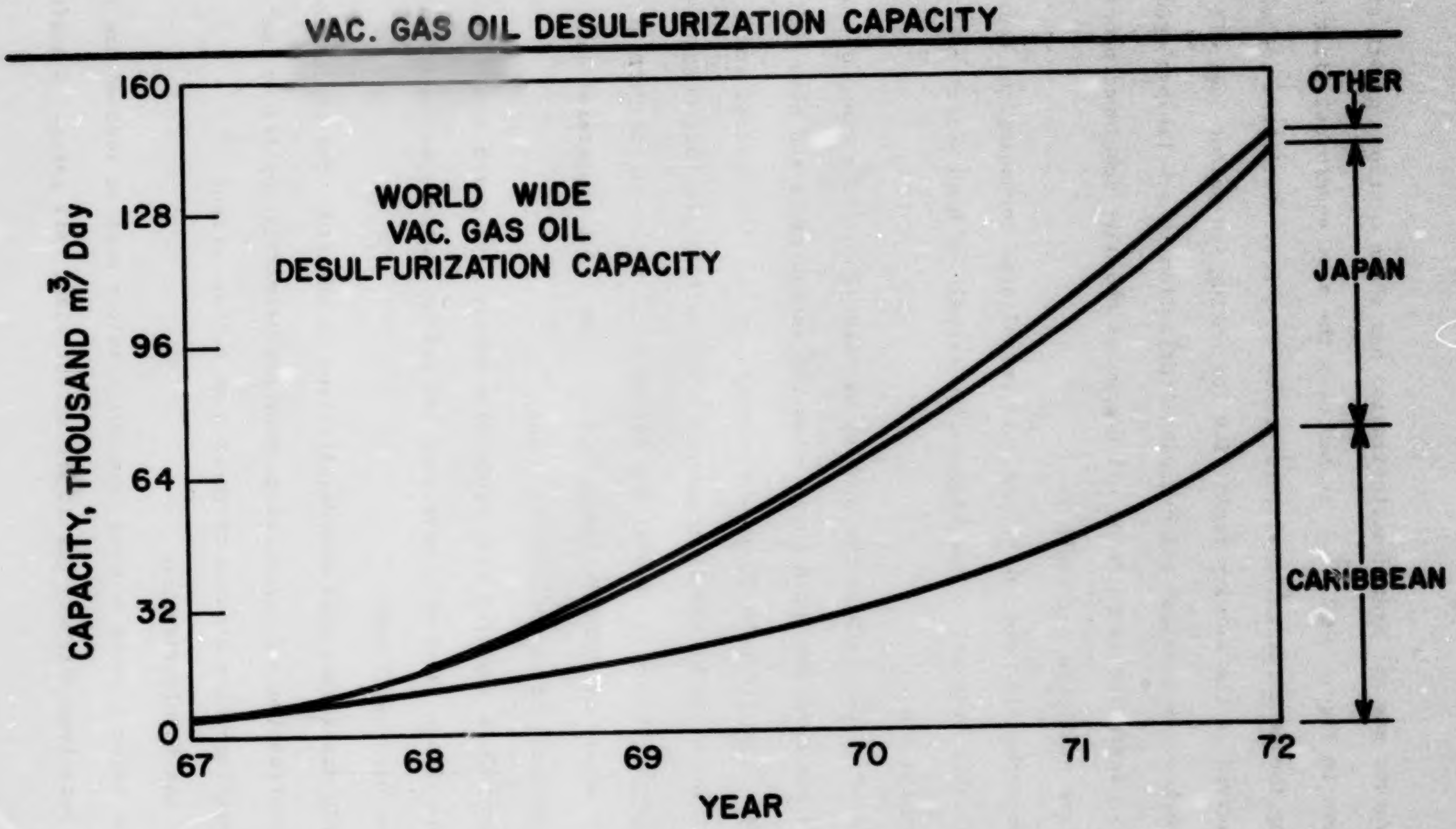


Figure 3-12. Vacuum gas oil desulfurization capacity.

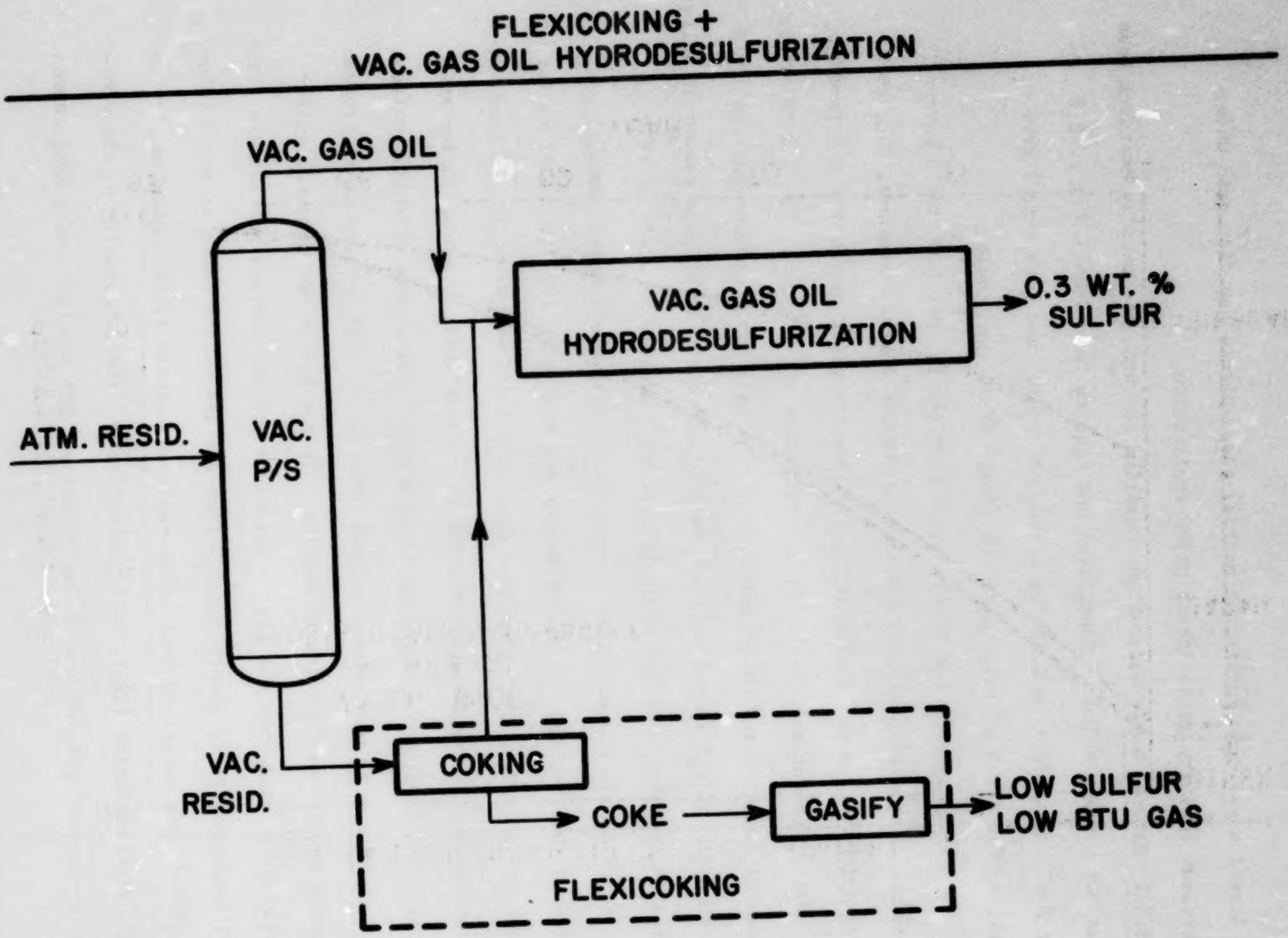

FLEXICOKING +
VAC. GAS OIL HYDRODESULFURIZATION
VAC. GAS OIL
ATM. RESID.
VAC.
P/S
VAC. GAS OIL
HYDRODESULFURIZATION
0.3 WT. %
SULFUR
VAC.
RESID.
COKING
COKE
GASIFY
LOW SULFUR
LOW BTU GAS
FLEXICOKING

Figure 3-13. Vacuum gas oil desulfurization.

is itself a gas desulfurization method; these plants are discussed under petroleum refinery gases—their major application.

3.3.3.1 Natural Gas— Natural gas supplied to consumers usually contains less than 0.1 percent sulfur. Specifications require less than 5.8 mg of H_2S per N m^3 (equivalent to 0.28 μg of SO_2 per joule) and less than 0.690g of total sulfur per N m^3 (equivalent to 37 ng of SO_2 per joule).

At the well-head, H_2S levels range from 140 μg per N m^3 to 75 percent by volume. Several processes are used to remove sulfur compounds, CO_2, and water from the raw gas (Table 3-10). These processes remove the H_2S from the gas with a sorbent and then strip to regenerate the sorbent. The H_2S is either flared or is converted to elemental sulfur using a Claus system (Section 3.3.3.2). The quantity of H_2S flared compared to that processed to produce elemental sulfur in the United States is not accurately known. However, a study of 1970 gas processing in six states, which produce about half the domestic natural gas, indicated that perhaps 710 Mkg of sulfur are recovered and 3.1 Gkg of sulfur oxides are flared to the atmosphere from United States gas wells.[35] Thus, although natural gas is usually regarded as a clean fuel, its preparation and delivery can involve the emission of substantial quantities of sulfur oxides.

3.3.3.2 Refinery Gases —As discussed previously, many process units produce offgases which contain hydrogen sulfide. If the H_2S is not removed, sulfur dioxide is emitted when the gas is burned in process heaters and boilers. The usual treatment is to absorb the H_2S from the gas stream using an amine solution.[36,37] The solutions most often employed contain either monoethanolamine (MEA), diethanolamine (DEA), or triethanolamine (TEA), depending on the properties of the sour gas, with a 10- to 20-percent DEA solution being most common.

Table 3-10. COMMERCIAL ACID - GAS TREATING PROCESSES IN THE UNITED STATES IN NATURAL GAS SERVICES

Process	Process description and comments	Number of plants
Benfield	Hot potassium carbonate is used to absorb CO_2 and H_2S. Applicable to gas with high CO_2 content.	18
Diglycolamine or Econamine	Amine-based process. Applicable to acid gas removal when a minimum of 1.5 to 2 percent acid gas is present.	15
Fluor solvent	Process based on the use of propylene carbonate, glyceral triacetate, and other glycerol acetate derivatives as absorbents. Process operates at ambient temperatures.	6
Girbitol or MEA	Absorption of H_2S is accomplished in a concentrated aqueous solution of alkanolamines.	200
Molecular sieves	Molecular sorption of H_2S and CO_2. Effective for low H_2S concentrations.	—
Selexol	Used on high CO_2-low H_2S gases.	6
Sulfinol	Amine-based process using diisopropanolamine and sulfolane.	37

In scrubbing, the amines react with H_2S to form compounds that can be decomposed by heat. This reversible reaction is

$$RNH_2 + H_2S \leftrightarrow RNH_3HS ,$$

where R is an organic radical. The amine scrubbing process (Figure 3-14) is a continuous operation in which sour gas is desulfurized by the lean amine solution in an absorber, the rich amine solution is regenerated by steam stripping in a separate unit, and the acid gas is sent to a sulfur recovery system. A properly operated amine treating unit can reduce H_2S content of the gas to less than 0.23 g H_2S/Nm^3.[38]

Upsets in the amine scrubbing system or in the sulfur plant can release hydrocarbons and H_2S; emissions are controlled by releasing these sulfur-rich gases to a flare system. A well-designed and properly maintained sulfur plant will reduce the frequency of emergency releases of gas to the flare.

Although the performance of amine scrubbing units has been well established by over 30 years of operation, new processes which employ other scrubbing media are emerging for refinery gas processing. Modified versions of some of the processes for removal of H_2S from sulfur plant tail gases are applicable; among these are the Giamarco-Vetrocoke (G-V) and Stretford processes, both of which feature an oxygen carrier to utilize aerobic oxygen for direct conversion of H_2S to elemental sulfur.[39]

Various caustic and sulfuric acid treatments are used to remove H_2S and mercaptans from distillates.[40,41] These are primarily used in conjunction with other treatment processes such as sweetening and are normally used in the final stages of refining. The quantities of sulfur removed are small in comparison with total refinery sulfur balance.

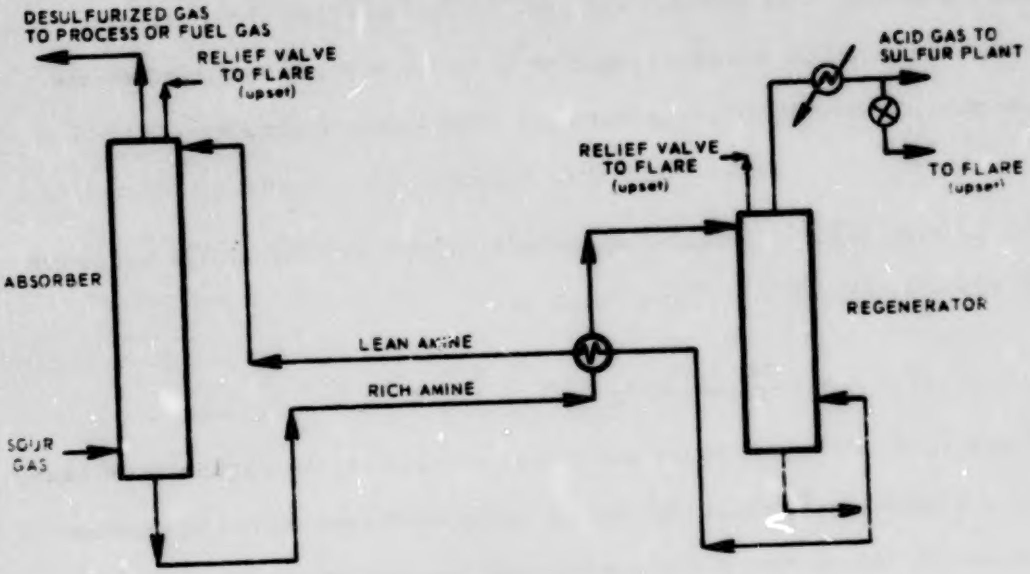

DESULFURIZED GAS TO PROCESS OR FUEL GAS
RELIEF VALVE TO FLARE (upset)
ACID GAS TO SULFUR PLANT
RELIEF VALVE TO FLARE (upset)
TO FLARE (upset)
ABSORBER
REGENERATOR
LEAN AMINE
RICH AMINE
SOUR GAS

Fig. 3-14. Flowchart for H_2S removal by amine solutions.

Sulfur recovery facilities are becoming an essential part of refinery operations because of the need to reduce both the sulfur content of refined products and the sulfur oxides emissions. Western production of recovered sulfur increased from 7.2 Gkg in 1969 to 8.1 Gkg in 1970 largely because of the increased supply of H_2S from refinery and natural gases. This compares with a total sulfur production from all sources of 16.1 Gkg in 1970.[42]

The Claus process (developed about 1890) is the most widely used method of producing sulfur from hydrogen sulfide.[43] The modified Claus process (developed about 1937) produces sulfur by first converting one-third of the hydrogen sulfide feed to SO_2 by controlled combustion of air,

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O ,$$

and then by reacting the products of combustion with the two-thirds unreacted feed in the presence of a suitable catalyst,

$$2H_2S + SO_2 \xrightarrow{\text{catalyst}} aS_2 + bS_6 + cS_8 + 2H_2O .$$

The letters a, b, and c represent the number of mols of the various molecular forms of sulfur vapor.[43] Although sulfur vapor is formed in the combustion reaction and in the catalytic conversion, the required amount of oxygen is that which will oxidize one-third of the hydrogen sulfide in the acid gas feed.[44] After each reaction, the sulfur vapor is condensed and allowed to drain to sulfur storage.

In one type of modified Claus sulfur recovery plant (Figure 3-15), the total acid gas stream enters the reactor and waste heat boiler where one-third of the acid gas is burned in a controlled amount of air. The exothermic reaction produces steam and sulfur vapor; the latter is condensed

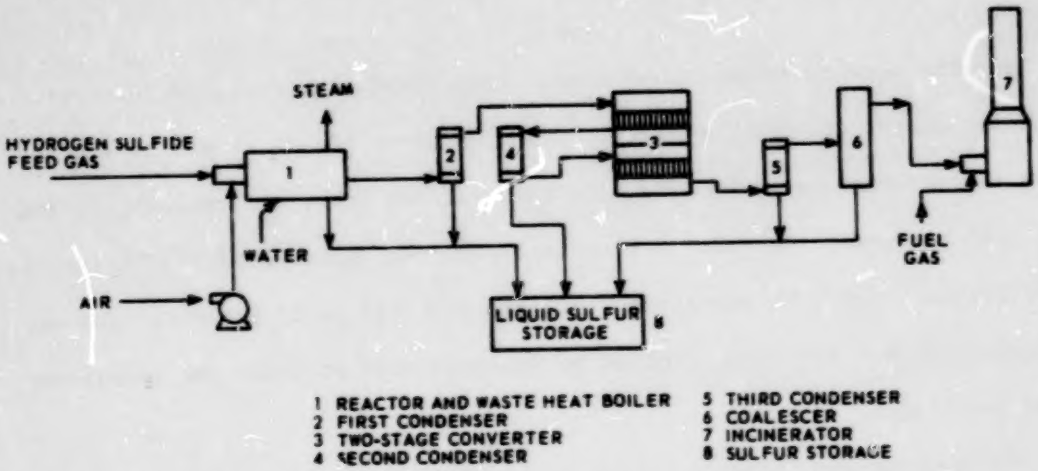

STEAM
HYDROGEN SULFIDE FEED GAS
1
2
3
4
5
6
7
WATER
AIR
LIQUID SULFUR STORAGE
8
FUEL GAS
1 REACTOR AND WASTE HEAT BOILER
2 FIRST CONDENSER
3 TWO-STAGE CONVERTER
4 SECOND CONDENSER
5 THIRD CONDENSER
6 COALESCER
7 INCINERATOR
8 SULFUR STORAGE

Fig. 3-15. Sulfur recovery plant (flowchart).

in the first condenser and drained to storage. Uncondensed gases go to the two-stage converter, in which some of the hydrogen sulfide is catalytically converted to more sulfur vapor. (The converter feed is elevated to the optimum temperature [510 K] by mixing with hot gas [750 K] from the reaction furnace.) The sulfur vapor formed by the first converter is condensed by the second condenser. Uncondensed vapors, before entering the second stage of the converter, are mixed with hot gas from the reaction furnace; they then pass to the third condenser and to a coalescer which removes entrained sulfur droplets. From the coalescer the gases go to an incinerator where residual sulfur compounds are converted to SO_2, diluted with air, and discharged to the atmosphere.

Bauxite appears to be the most desirable catalyst because of low cost, high durability, and high activity.[43] The catalyst bed thickness is limited since the reaction is exothermic, low temperatures favor the conversion, and heat must be easily removed. A one-stage plant can operate with efficiencies of 85 percent, but with two stages, efficiencies can be 95 percent. For air pollution control all plants should be designed with at least two catalytic converter stages.

For minimum discharge of sulfur compounds and maximum conversion of sulfur, the initial stoichiometric ratio should be 2 mols of hydrogen sulfide to 1 mol of SO_2. To maintain this ratio, the correct amount of air must be metered into the reaction furnace. Figure 3-16 shows what happens when the correct amount of air is not supplied.[45] For example, if the initial ratio is 1.3 to 1, instead of 2 to 1, the ratio will decrease as the conversion increases until 84.8 percent maximum conversion is attained.[44] Sophisticated instrumentation systems that adjust the flow of air to maintain optimum conditions are available.[46]

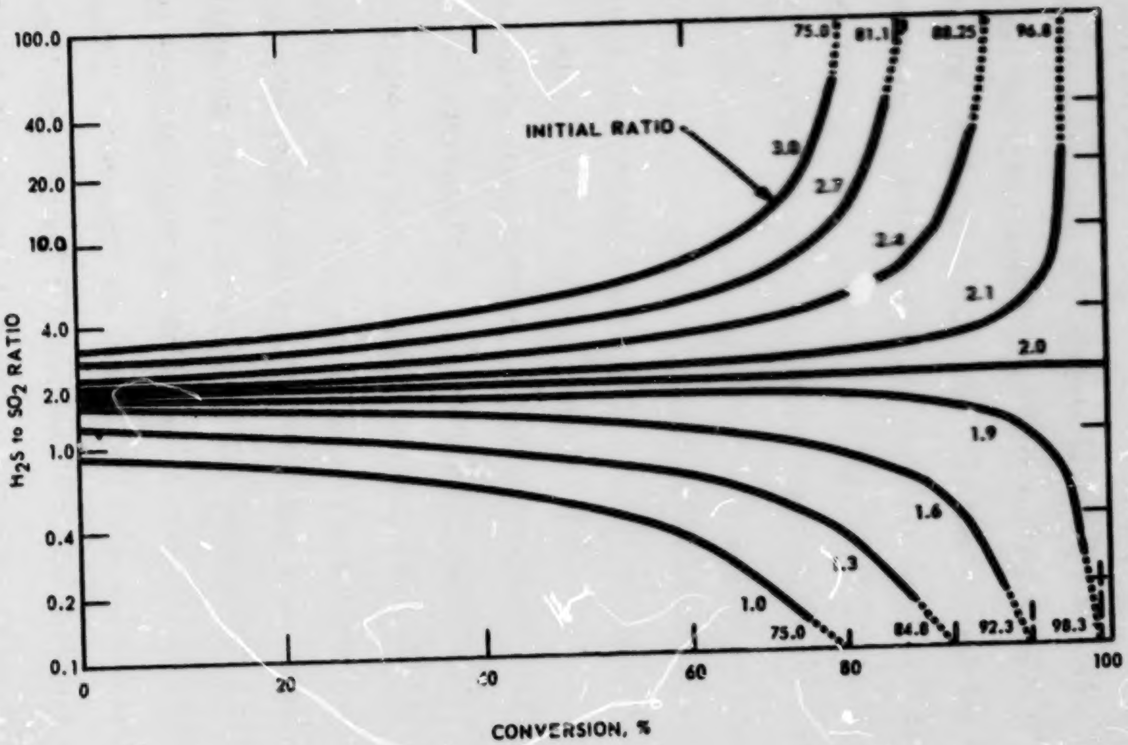


Fig. 3-16. Variation of H_2S to SO_2 ratio with conversion and maximum theoretical conversion possible at specified ratio.

3.3.3.3 Claus Plant Tail Gases-- There are two essential elements in the tail gas desulfurization problem: economics and concentration. Increasing the efficiency of a chemical reaction becomes more difficult (and expensive) as the efficiency approaches 100 percent.

The selection of a process for sulfur removal from Claus plant effluents is dependent on several considerations: the maximum permissible SO_2 concentration in the final gas stream, the condition and composition of the stream to be treated, the end use for the product, the system reliability, and the operating cost. Selection of a process thus depends on the point of application--that is, before or after the sulfur plant incinerator (Item 7, Figure 3-15). Incinerator feed varies from about 0.6 to 3.0 weight percent sulfur content (dry basis) and contains nitrogen, carbon dioxide, hydrogen, carbon monoxide, hydrocarbons, oxygen and water vapor, carbonyl sulfide (COS), carbon disulfide (CS_2), hydrogen sulfide, sulfur dioxide, sulfur vapor (S_2 and S_8), and entrained sulfur mist. In incinerator product, all sulfur occurs as SO_2; other compounds are oxygen, nitrogen, carbon dioxide, and water vapor.

Listed in Table 3-11 are seven clean-up processes which are either being installed or are in operation in processing plants.[47] These techniques, developed by private industry, represent only a sample of at least 40 to 50 processes for desulfurizing sulfur plant tail gases, stack gases, and other effluent streams.[48] Processes 1 through 4 operate on the Claus unit tail gas and replace the usual incineration step. The Beavon and Clean Air processes (1 and 2) both employ a Stretford unit for conversion of H_2S to sulfur. The IFP and Sulfreen processes employ catalysts to extend the Claus reaction. Processes 5 through 7, though different, all operate on incinerator effluent and are basically SO_2 removal systems. Stack gas cleaning is discussed further in Section 3.4.

One of the methods applicable to the Claus unit tail gas (rather than to the incinerator effluent) is the Beavon process (Figure 3-17).[49] First, all sulfur is converted to H_2S by catalytic hydrolysis and hydrogenation. The water vapor and excess hydrogen gas in the tail gas stream are usually sufficient to sustain these reactions. The gas mixture is then cooled, and condensed water is removed. Next, hydrogen sulfide is extracted from the tail gas using the Stretford process. The Stretford process reacts sodium carbonate solution with H_2S to form sodium hydrosulfide, which is then oxidized to sulfur by sodium vanadate, also in solution. Subsequently, the reduced vanadium is re-oxidized to the pentavalent state by blowing with air containing an oxidation catalyst (sodium anthraquinone disulfonate). Finally, sulfur is skimmed off of the solution, washed, dried by centrifuging or filtration, and added to the product from the parent sulfur plant.[49]

Other clean-up processes may be equally effective, or even more appropriate, depending on effluent characteristics and economic considerations.

A sulfur plant should be designed to prevent as many operating difficulties and shutdowns as possible, and standby equipment should be installed. For these refineries a standby sulfur recovery train is necessary to permit uninterrupted operation and compliance with air quality regulations.[50]

Sulfur plants typically recover 90 to 95 percent of the entering sulfur, with the remaining 5 to 10 percent being lost to the atmosphere as sulfur dioxide. Large units of the latest design will recover about 97 percent of the sulfur and lose only 3 percent.[49] Unfortunately, even with these relatively high recovery efficiencies, SO_2 tail gas concentrations are about 1.5 percent.[51] The recovered sulfur is usually marketed.[46]

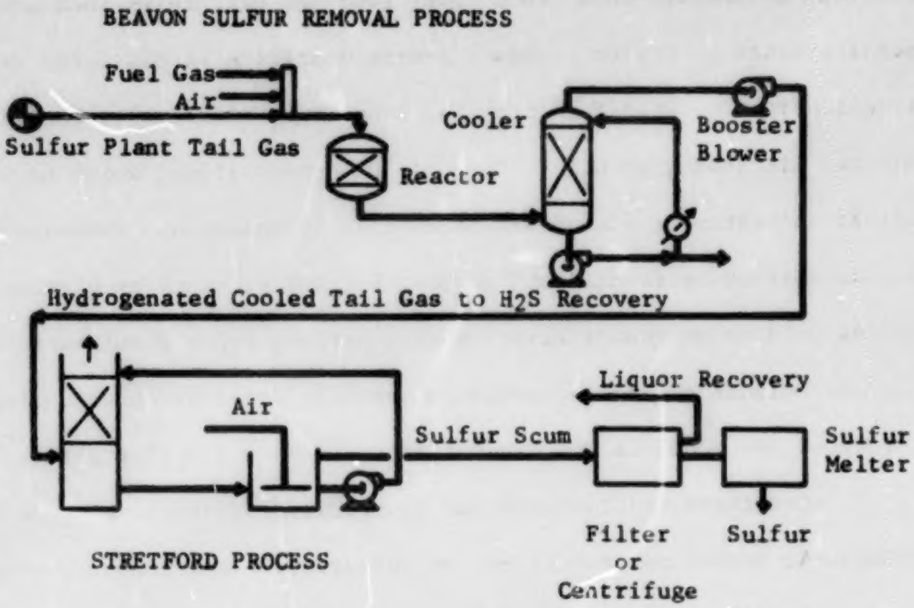

BEAVON SULFUR REMOVAL PROCESS
Fuel Gas
Air
Sulfur Plant Tail Gas
Reactor
Cooler
Booster
Blower
Hydrogenated Cooled Tail Gas to H2S Recovery
Air
Sulfur Scum
Liquor Recovery
Sulfur
Melter
Sulfur
Filter
or
Centrifuge
STRETFORD PROCESS

Fig. 3-17. Flow diagram of processes to eliminate air pollutants from tail gases of sulfur plants.

3.4 FLUE GAS DESULFURIZATION

3.4.1 Flue Gas Desulfurization Processes

Since the application of gas washing systems to power plants in the British Isles in the early 1930's, the number of installed systems has increased significantly. There is a wide variety of processes currently installed or in various stages of construction of planning. Processes differ with respect to the techniques employed to remove the sulfur oxides from the combustion gases and methods employed which produce wastes or useful products. Sulfur oxides emission control processes are categorized as follows:

1. Limestone to boiler
2. Limestone to scrubber
3. Lime to scrubber
4. Sodium compounds to scrubber
5. Magnesium compounds to scrubber
6. Direct conversion to acid
7. Catalyzed weak sulfuric acid scrubbing
8. Activated carbon adsorption

In addition, fly ash scrubbers are installed or planned which desulfurize flue gases incidental to removal of particulate matter from the gas stream. Tabulations of United States and foreign sulfur oxides emission control systems are given in Tables 3-12 and 3-13, respectively. Process sheets 3-1 through 3-19 present more detailed information on some of these systems.

3.4.1.1 Limestone to Boiler Processes--Process 3-1 through 3-5 describe limestone to boiler processes installed in the United States. Although operating experience has been poor and one of the systems has been abandoned, plans for operation of the remainder of these systems are continuing. All of these systems except one are designed to operate on a closed liquor loop basis except for any seepage which may occur from unsealed settling ponds. The system at the Shawnee Power Plant operates without a scrubber as described in Process 3-2. The solids from these systems require disposal.

3.4.1.2 Limestone to Scrubber Processes—Various limestone to scrubber processes are described in Processes 3-1 through 3-9. The Battersea, Bankside, and Key West processes described in Processes 3-6, 3-7, and 3-9 operate on an open loop basis with some wastewater treatment. The Battersea Power Station oxidizes part of the liquor to convert sulfites to sulfates. All of the plants except the Bankside Power Station settle solids from the liquor prior to discharge. The Will County Power Plant system operates on a closed loop basis except for any seepage which may occur from the unlined settling pond. The solids from all systems are wasted.

3.4.1.3 Lime to Scrubber Processes--Processes 3-10, 3-11, and 3-12 describe major lime to scrubber processes installed outside of the United States. As shown in Table 3-12, lime to scrubber processes are soon to be (if not already) activated in the United States. Non United States experience with these systems has been excellent. One system operates on a completely closed liquor loop basis producing a usable gypsum product as described in Process 3-12. Others operate on a closed loop basis except for any seepage which may occur from unsealed settling ponds. The solids from these latter systems require disposal.

3.4.1.4 Sodium Compounds to Scrubber--There are several different sodium compound scrubbing systems. The sodium compounds may be regenerated by thermal or chemical techniques, may be wasted, or may be produced for sale depending upon the economics involved. The efficiency of these systems exceeds 90 percent.

Sodium solution scrubbing with thermal regeneration--The thermal regeneration type process is described in Process 3-13. The SO_2 produced by

Table 3-11. - SOME PROCESSES USED FOR SULFUR REMOVAL FROM CLAUS TAIL GAS[47]

Name	Developer	Reference	Point of application/technique	Extraneous process Feed streams required	Sulfur removal	Product
1. Beavon Sulfur Removal Process	Ralph M. Parsons and Union Oil Co. of California	47,52,53	Claus unit tail gas/ converts sulfur compounds to H_2S, H_2S to sulfur	Fuel gas and air	250 ppm or less	Sulfur
2. Clean Air Sulfur Process	J. F. Pritchard and Co. and Texas Gulf Sulfur Co.	54,55	Claus unit tail gas/ converts sulfur compounds to H_2S, H_2S and SO_2 to sulfur	Fuel gas and air	250 ppm or less	Sulfur
3. IFP Sulfur Recovery Process	Institut Francais du Petrole	56,57	Claus unit tail gas/ extends Claus process	None	1 000 ppm	Sulfur
4. Sulfreen Process	SNPA and Lurgi Gesellschaften	58,59,60	Claus unit tail gas/ extends Claus process	Inert gas for regeneration	85% of sulfur in the Claus plant tail gas	Sulfur
5. Shell's Flue Gas Desulfurization Process	Koninkiijke/Shell Laboratorium, The Netherlands	61	Incinerator flue gas/ dry process for SO_2 removal	Reducing gas H_2, H_2/CO mixtures, or light paraffinic hydrocarbons	90%	SO_2 formed is recycled through a Claus unit
6. SNPA-Sulfuric Acid Process	NSPA and Haldor Topsoe	58,59	Incinerator flue gas/ wet contact acid process for SO_2 removal	Fuel gas and air	90% SO_2 conversion	94% sulfuric acid
7. Wellman-SO_2 Recovery Process	Wellman Power Gas	52,62,63, 64	Incinerator flue gas/ SO_2 removal by solution method	None	100 ppm	60% SO_2 and 40% water vapor

Table 3-12. - U.S. SYSTEMS FOR CONTROL OF SO_2 IN COMBUSTION GASES

Scrubber systems for coal-fired boilers									
Plant location by type of control system	Supplier of described system	Start-up date		Control system performance					Solid waste disposal method
		Under construction (anticipated)	In operation	Size of unit MW[1]	Gas flow rate m^3/s	Removal efficiency, %		Sulfur in fuel	
						SO_2	particulates		
Limestone to scrubber									
Commonwealth Edison, Will County Station	Babcock & Wilcox: 2 parallel systems, venturi/TCA in series	--	2/72	163	360	70 - 90	98	4.0	Concentrated to about 35% in 20.2 km^2 pond
Kansas City Power & Light Hawthorne Unit No. 4	Combustion Engineering: shut down late 1972 for conversion to modified tail and addition system	--	8/72	100	NA	70	99 to 1.77 g/Nm^3	3.5	Ash pond
City of Key West, Stock Island Station	Zurn Air Systems: 2 single-stage parallel inspirating venturi	--	2/73	37	74 at 450 K	85	95	2 - 3	Landfill for settled solids; clarified liquor to ocean
Kansas City Power & Light La Cygne Station	Babcock & Wilcox: 7 parallel systems, venturi/sieve plate columns in series	12/72	late 1973	850	NA	80	98.7	5.0	Ash pond
Arizona Public Service, Cholla Station	Research-Cottrell: flooded disc venturi in series with packed absorber	early 1973	--	115	220 at 416 K	--	--	1.0 (12%-18% ash)	Ash pond
Tennessee Valley Authority, Widows Creek	Undecided; 4 trains, downdraft venturi, open grid tower	early 1975	--	550	750 at 344 K	80	>99	3.7 (16% ash)	Ash pond; liquor recirculated
Northern States Power Co., Sherborne County Station Unit 1	Combustion Engineering: 12 single-stage marble bed scrubbers/unit, 24 total scrubbers	1975	--	680	NA	50	99	1.0	Ash pond; liquor recirculated
Southern California Edison, Navajo Station first installation	Undecided	6/75	--	750	NA	--	--	0.3	Ash pond

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[1] Unless otherwise indicated.

Table 3-12. - U.S. SYSTEMS FOR CONTROL OF SO_2 IN COMBUSTION GASES
(Continued)

Plant location by type of control system	Supplier of described system	Scrubber systems for coal-fired boilers (continued)							
		Start-up date		Control system performance					Solid waste disposal method
		Under construction (anticipated)	In operation	Size of unit MW[1]	Gas flow rate m^3/s	Removal efficiency, %		Sulfur in fuel	
						SO_2	particulates		
Southern California Edison, Navajo Station second installation	Undecided	9/75	—	750	NA	—	—	0.5	Ash pond
Northern States Power Co., Sherborne County Station Unit 2	Combustion Engineering: 12 single-stage marble bed scrubbers/unit, 24 total scrubbers	1976	—	680	NA	50	99	1.0	Ash pond; liquor recirculated
Southern California Edison, Navajo Station third installation	Undecided	6/76	—	750	NA	—	—	0.5	Ash pond
Detroit Edison, St. Clair Station	Peabody Engineering: 2 parallel Lurgi venturis in series with tray scrubbers	—	—	180	NA	82	99	3.7 (16% ash)	Clamshelled from pond to open area
Union Electric, Meramec Station No. 1	Combustion Engineering: 2 single-stage marble bed scrubbers	—	—	110	NA	to 0.52 µg/J	99	3.0 (10% ash)	Ash pond; liquor recirculated
Limestone to boiler									
Union Electric Company, Meramec Station No. 2	Combustion Engineering: 2 parallel single-stage marble bed scrubbers	—	9/68-12/71	140	NA	50 - 70	99	3.0 (10% ash)	Ash pond; liquor recirculated
Kansas Power and Light, Lawrence Station No. 4	Combustion Engineering: 2 marble bed scrubbers/125-MW unit; 6 marble bed scrubbers	—	12/68	125	NA	50 - 65	—	3.5 (12% ash)	Ash pond; liquor recirculated

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[1] Unless otherwise indicated.

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Table 3-12. - U.S. SYSTEMS FOR CONTROL OF SO_2 IN COMBUSTION GASES
(Continued)

Scrubber systems for coal-fired boilers (continued)									
		Start-up date		Control system performance					
						Removal efficiency, %			
Plant location by type of control system	Supplier of described system	Under construction (anticipated)	In operation	Size of unit MW^1	Gas flow rate m^3/s	SO_2	particulates	Sulfur in fuel	Solid waste disposal method
Lime to scrubber									
Louisville Gas & Electric, Paddy's Run Station	Combustion Engineering: 2 single-stage marble bed scrubbers	—	3/73	70	NA	80 to 0.52 µg/J	99	3.5	Rotary-driven filter; solids to landfills
Duquesne Light Company, Phillips Station	Chemico: 2-stage venturi	spring 1973	—	100	212 at 456 K	80	>99	2.0	Sym Earth process in inert landfill
Sodium sol'n (therm. regen.)									
Nevada Power Company, Reid Garner Station Nos. 1 and 2	Combustion Equipment Associates: each unit, 1 venturi impingement tray separator, radial vane demister	early 1973	—	125 125	NA NA	90 90	>98 >98	0.5 - 1.0 (6% ash)	Treated at Trona salt-mining site; solar evaporation pond
General Motors Chevrolet/Parma, Ohio	General Motors: 4 valve tray scrubbers	late 1973	—		71 at 322 K	—	—	—	—
Northern Indiana Pub. Service, D. H. Mitchell Station Unit 11	Wellman Power Gas: 3- or 4-stage valve tray absorber	mid 1974	—	115	146	90 to 200 ppm	to 0.52 µg/J	3.5 (11.5% ash)	Elemental sulfur stockpiled or sold
MAGOX (therm. regen.)									
Philadelphia Electric Co., Eddystone Station	[1] Peabody Engineering: 3-stage venturi rod	mid 1973	—	3 at 120, 1 unit SO_2 controlled	NA	90	—	2.5 (5% ash)	Acid sold
Potomac Electric Co., Dickerson Station No. 3	Chemico: 2-stage venturi	early 1974	—	100	139 at 455 F	90	90 to 0.09 g/Nm^3	3.0	Regenerate MgO; produce H_2SO_4

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[1] Unless otherwise indicated.

Table 3-12. - U.S. SYSTEMS FOR CONTROL OF SO_2 IN COMBUSTION GASES
(Continued)

Scrubber systems for coal-fired boilers (continued)

Plant location by type of control system	Supplier of described system	Start-up data		Control system performance					Solid waste disposal method
		Under construction (anticipated)	In operation	Size of unit MW[1]	Gas flow rate m^3/s	Removal efficiency, %		Sulfur in fuel	
						SO_2	particulates		
Direct conversion to acid									
Illinois Power Company, Wood River Station	Monsanto: reheat system	—	10/72	100	171 at 427 K	85	100	3.3 (11-12% ash)	Acid sold
Ash slurry									
Minnesota Power & Light, Aurora Station	Krebs Engineering: 1-stage rod deck	—	5/71	60 60	118, 118 at 327 K	—	—	—	—
Public Service of Colorado, Valmont Station No. 5	Air Correction Div., UPO: 2 parallel 3-stage TCA's	—	10/71	190	218	40	0.05 g/Nm^3	0.8	Ash slurry
Pacific Power & Light, Dave Johnson Station	Chemico: 3 parallel venturis	—	early 1972	330	705 at 405 K	40	99.8	0.4 (14% ash)	Ash pond
Public Service of Colorado, Cherokee Station No. 3	Air Correction Div., UPO: 3-stage TCA	—	10/72	150	287	20	0.09 ng/J	0.5 (9% ash)	Ash pond
Public Service of Colorado, Araphoe Station No. 4	Air Correction Div., UPO: 4 parallel 3-stage TCA's	—	9/73	100	245	35	0.05 g/Nm^3	0.8 (7% ash)	Ash slurry
Minnesota Power & Light, Clay Boswell Station Unit 3	Krebs Engineering: 1-stage rod deck	1/73	—	350	892 at 327 K	—	0.05 ng/J	0.7 (10-11% ash)	—
Duquesne Power & Light, Phillips Station	Chemico: 3 parallel venturis	2/73	—	387 (300 controlled)	567 at 455 K	—	—	—	—
Duquesne Power & Light, Elrama Station	Chemico: 5 parallel single-stage venturis	2/73	—	494	1038 at 426 K	—	—	—	—
Public Service of Colorado, Cherokee Station No. 1	Air Correction Div., UPO	6/73	—	130	245	20	0.09 ng/J	0.5 (9% ash)	Ash pond

---

[1] Unless otherwise indicated.

Table 3-12. - U.S. SYSTEMS FOR CONTROL OF SO_2 IN COMBUSTION GASES
(Continued)

Plant location by type of control system	Supplier of described system	Start-up date		Control system performance					Solid waste disposal method
		Under construction (anticipated)	In operation	Size of unit MW[1]	Gas flow rate m^3/s	Removal efficiency, %		Sulfur in fuel	
						SO_2	particulates		
Scrubber systems for coal-fired boilers (continued)									
Public Service of Colorado, Cherokee Station No. 4	Air Correction Div., UPO: 4 parallel 3-stage TCA's	8/74	--	350	716	20	8.6 ng/J	0.5 (9% ash)	Ash pond
Philadelphia Electric Co., Eddystone Station	Peabody Engineering: 2-stage venturi rod	--	--	3 at 120, 2 units ash controlled	--	--	--	2.5 (9% ash)	----
Arizona Public Service, Four Corners Station	Chemico: 2 venturi/unit	--	--	575	1256 at 380 K	--	--	0.75 (25% ash)	----
Pennsylvania Electric, Holtwood Station	Chemico: 1 single-stage venturi	--	--	72	165 at 455 K	--	--	---	----
Scrubber systems for oil-fired boilers									
MAGOX (therm. regen.)									
Boston Edison Company, Mystic Station No. 6	Chemico: 1 single-stage venturi	--	4/72	150	208 at 422 K	90	$0.04\ g/Nm^3$	2.5	MgO regenerated; H_2SO_4 produced

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[1] Unless otherwise indicated.

Table 3-13. - NON-U.S. COMBUSTION GAS SO_2 EMISSION CONTROL PROCESSES

Item no.	Developer, manufacturer, country	Purchaser	Controlled process and gas flow rate	Comments and date of startup
			LIME OR LIMESTONE SLURRY SCRUBBING	
1	Custom designed (London, England)	Battersea Power Station	14 coal- and 1 oil-fired boiler, 509 Mw	Sludge discarded, open loop (1932).
2	Howden-I.C.I. Swansea, Wales)	Tir John Power Station	Utility boilers	System abandoned after failure to fulfill design plans (1935).
3	Howden-I.C.I. (London, England)	Fulham Power Station	Utility boilers	Closed loop; shut down for security reasons at onset of World War II; not reactivated; sludge discarded (1936).
4	Custom designed (London, England)	Bankside Power Station	5 oil-fired boilers 300 Mw	Sludge discarded, open loop (1952).
5	Bahco (Sweden)	Unknown	3 oil-fired boilers	Sludge discarded (Nov. 1969).
6	Mitsui/Chemico (Japan)	Mitsui Aluminum	Coal-fired boiler 140 Nm^3/s	Sludge discarded (Mar. 1972).
7	Mitsubishi (Japan)	Kansai Electric Power	Oil-fired boiler 28 Nm^3/s	Byproduct gypsum (Apr. 1972).
			SODIUM SOLUTION THERMAL REGENERATION	
8	Wellman Power Gas and Mitsubishi (Japan)	Japan Synthetic Rubber	Oil-fired boiler 50 Nm^3/s	Byproduct sulfuric acid (1971).
9	Wellman Power Gas and Mitsubishi (Japan)	Chubu Power Station	220-Mw, oil-fired boiler	Planned startup date unknown; product unknown.

Table 3-13. - NON-U.S. COMBUSTION GAS SO_2 EMISSION CONTROL PROCESSES (continued)

Item no.	Developer, manufacturer, country	Purchaser	Controlled process and gas flow rate	Comments and date of startup
			SODIUM SOLUTION LIME OR LIMESTONE REGENERATION (DOUBLE ALKALI)	
10	Showa Denku (Japan)	Unknown	Oil-fired boiler 236 m^3/s	Planned to produce gypsum; status of marketability unknown (June 1973).
			SODIUM SOLUTION - NO REGENERATION	
11	Jinkoshi-Nippon Kokan (Japan)	Oji Paper Co.	Oil-fired boiler 17 m^3/s	Produces sodium sulfite and bisulfite liquor for partial reuse for paper production (1969).
12	Showa Denku (Japan)	Unknown	Oil-fired boiler 61 m^3/s	Produces sodium sulfite solution for sale to paper industry (late 1970).
13	Kureha Chemical Industry Co., Ltd. (Japan)	Mitsui-Toatsu Chemical Co.	Oil-fired boiler 75 m^3/s	Produces sodium sulfite (Sept. 1971).
14	Kureha Chemical Industry Co., Ltd. (Japan)	Kohnan Utility	Oil-fired boiler 85 m^3/s	Produces sodium sulfite (late 1972).
15	Jinkoshi-Nippon Kokan (Japan)	Oji Paper Co.	Oil-fired boiler 236 m^3/s	Plans for use of product unknown (1973).
16	Kureha Chemical Industry Co., Ltd. (Japan)	Oji Paper Co.	2 oil-fired boilers 123 m^3/s each	Produces sodium sulfite for marketing; startup date unknown.
17	Showa Denku (Japan)	Unknown	Unknown 33 m^3/s	Produces sodium sulfite; startup date unknown.

Table 3-13. - NON-U.S. COMBUSTION GAS SO_2 EMISSION CONTROL PROCESSES

Item no.	Developer, manufacturer, country	Purchaser	Controlled process and gas flow rate	Comments and date of startup
CATALYZED WEAK SULFURIC ACID SCRUBBING				
18	Chiyoda Chemical Engineering and Construction Co., Ltd. (Japan)	Fuji Kosan Co.	Oil-fired boiler 63 m^3/s	Planned to produce gypsum; status of marketability unknown; startup date unknown.
19	Chiyoda Chemical Engineering and Construction Co., Ltd. (Japan)	Mitsubishi Rayon Co.	Oil-fired boiler 36 m^3/s	Planned to produce gypsum; status of marketability unknown; startup date unknown.
ACTIVATED CARBON ABSORPTION-DESORPTION				
20	Sumitomo Shipbuilding and Machinery Co. (Japan)	Sakai Power Station	Oil-fired boiler 71 m^3/s	Produces 98 percent sulfuric acid (Feb. 1972)
21	Hitachi, Ltd.	Kashima Power Station	Oil-fired boiler 182 m^3/s (partial control)	Produces gypsum for sale; startup date unknown.
AMMONIA SCRUBBING				
22	State Research Inst. Gas Cleaning (USSR)	Unknown	Coal burning 39 Nm^3/s	Shut down in 1961 when station was converted to gas (1952).

regeneration may be marketed as such or converted to sulfuric acid, sulfur, or gypsum which is either sold or wasted according to the economics involved. With the current state of development, some sulfur compounds are purged from the scrubber liquor system. It is possible that Federal or other regulations would not permit discharge of this purge stream without further treatment.

Sodium solution scrubbing with lime or limestone regeneration[65] -- The SO_x is scrubbed from carrier gases with solutions of sodium carbonate or sodium hydroxide. The resulting sodium sulfite solution is regenerated with lime or limestone to produce recycle sodium hydroxide and a calcium sulfite-sulfate waste sludge which is separated from the liquor as such or is oxidized prior to separation to convert sulfites to sulfates.

A simplified version of the chemistry of the absorption and lime (CaO) regeneration for this process is indicated in the following equations:

$$NaOH + SO_2 \rightarrow NaHSO_3,$$

$$NaHSO_3 + CaO \rightarrow CaSO_3 + NaOH.$$

As of November 1972, no systems of this kind were in operation. One system is planned for installation in Japan which reportedly will produce gypsum.

Sodium solution scrubbing to produce sodium sulfite -- Some systems are designed to produce sodium sulfite as shown in Tables 3-12 and 3-13. These systems involve scrubbing the flue gas with recycled sodium carbonate or sodium hydroxide solutions to produce a concentrated liquor. In addition to the applications shown, 99-percent efficient sodium carbonate scrubbing has been applied world-wide for many years in conjunction with a process for producing purified carbon dioxide from boiler flue gas. When economically feasible, the liquor is marketed. Although in the past some systems have been disigned for liquor disposal to sewers and streams in the raw form or after oxidation to increase sulfate content, it is possible that this would not be permissible under Federal or other water pollution regulations.

3.4.1.5 Magnesium Compounds to Scrubber--An installed magnesium oxide scrubbing and regeneration system is described in Process 3-14. These systems are designed to avoid the production of wastes. The SO_2 produced may be marketed or wasted subject to much the same conditions as described in conjunction with the thermal regeneration of sodium compounds (Section 3.4.1.4).

3.4.1.6 Direct Conversion to Acid--An installation of this system is described in Process 3-15. This system is designed to avoid the production of wastes. The acid produced may be sold, converted to other salable products, or neutralized and wasted depending upon the economics involved.

3.4.1.7 Catalyzed Weak Sulfuric Acid Scrubbing--Based on pilot plant experience indicating 50 to 90 percent efficiency, a process is being applied in Japan as shown in Table 3-13. The process involves weak sulfuric acid scrubbing of flue gases. Normally SO_2 would have low solubility in weak sulfuric acid; however, with the use of a Fe+++ oxidizing catalyst dissolved in a nearly O_2-saturated liquid, SO_2-SO_3 gases are chemically complexed and partially oxidized so that the overall SO_2 solubility is greatly increased. Sulfuric acid bled from the scrubber liquor system is neutralized with limestone to produce gypsum crystals which are centrifuged from the liquor. The process operated on a completely closed loop basis.

3.4.1.8 Activated Carbon Adsorption--Installations of these systems are described in Processes 3-16 and 3-17. As described, wastewaters are involved in both the processes. The SO_2 produced by the dry desorption process may be marketed or wasted subject to much the same conditions as described in conjunction with the thermal regeneration of sodium compounds (Section 3.4.1.4)

3.4.1.9 Ash Slurry Scrubbing--Installations of ash slurry scrubbing systems are described in Processes 3-18 and 3-19. These systems involve waste-

Process 3-1. Limestone to Boiler Process[67]
Meramec Power Station
Union Electric Company
St. Louis, Missouri

PROCESS DESIGN DESCRIPTION

This process was retrofitted to handle the total flue gases from a 140-Mw, pulverized coal (3) percent sulfur, 10 percent ash) fired power boiler. The system is no longer in operation.

The system was designed for the injection of pulverized limestone into the boiler. Flue gases from the boilers flowed to two marble bed, absorber-type scrubbers installed in parallel. Gases from the scrubber flowed to a steam heater designed to reheat the flue gases to 350 K.

Flue gases were scrubbed with recycled liquor and necessary makeup water. Liquor from the scrubber flowed to a settling system where solids were removed and then pumped to an unlined settling pond.

STATUS OF OPERATION

Installation of the system was initiated in 1967, and the system was activated in the fall of 1968. The unit was shut down permanently in May 1971. The unit was never operated successfully for an extended period of time, the longest continuous run being 80 hours.

Operating problems involved blockage of flue gas flow through the boiler system and scrubber and excessive fan impeller vibration. Because of the limited extent of operations, experience with the plume reheat, sludge settling, and waste disposal components of the process was insufficient for any firm conclusions on the effectiveness or reliability of these systems.

Sulfur oxide removal efficiencies were about 50 to 70 percent, and particulate matter removal efficiences were of the order of 99 percent during the trial runs.

Process 3-2. Limestone to Boiler Process[67]
Shawnee Power Station
Tennessee Valley Authority
Paducah, Kentucky

PROCESS DESIGN DESCRIPTION

This process was retrofitted to handle the total flue gases from a 150-Mw, pulverized coal (2.7 percent sulfur, 15 percent ash) fired power boiler. The system is no longer operational.

The system was designed for the injection of pulverized limestone into the boiler. Flue gases from the boiler flowed to an electrostatic precipitator and then to the stack. Solids from the system were dumped.

The system was designed primarily for experimental studies.

STATUS OF OPERATION

Conceptual design studies were initiated in late 1967, followed by construction in 1969 and 1970. First testing was initiated in May 1970, and testing and operation was completed in January 1972. The longest continuous run was of the order of several days. Operations were hampered by blockage of flue gas flow through the boiler system. Sulfuric oxide removal efficiences varied from 17 to 36 percent, and particulate matter removal efficiences varied from 72 to 99 percent.

Process 3-3. Limestone to Boiler Process[68]
Lawrence Power Station, Unit Nos. 4 and 5
Kansas Power and Light Co.
Lawrence, Kansas

PROCESS DESIGN DESCRIPTION

Unit Nos. 4 and 5 are equipped with similar systems which utilize a common sludge settling pond. The system on Unit No. 4 is retrofitted to a 125-Mw pulverized coal (3.5 percent sulfur, 12.5 percent ash) fired power boiler. The system applied to Unit No. 5 was installed in conjunction with the erection of a new 420-Mw pulverized coal fired power boiler.

The systems are designed for injection of pulverized limestone into the boiler. Flue gases from the boilers flow to marble bed absorber-type scrubbers installed in parallel. Flue gases from the scrubbers flow to a steam heater which increases flue gas temperature prior to discharge.

The gases are scrubbed with recycled liquor and necessary makeup water. Liquor from the scrubbers flows to a common unlined settling pond and is then recycled to the scrubber system. Solids from these systems require disposal.

STATUS OF OPERATION

Construction of the system for Unit No. 4 was completed according to original plans about the first of December 1968. The system for Unit No. 5 was activated in early fall 1971. As of October 1972, neither system had performed according to design expectations. Corrosion and blockage of flue gas flow are some of the problems which have been encountered. Under these conditions, SO_2 removal efficiencies were of the order of 50 to 60 percent.

Process 3-4. Limestone to Boiler Process[67,69]
Hawthorne Power Station Unit Nos. 3 and 4
Kansas City Power and Light Co.
Kansas City, Missouri

PROCESS DESIGN DESCRIPTION

Unit Nos. 3 and 4 are retrofitted with similar systems and are 130-Mw pulverized coal (3.2 percent sulfur, 14 percent ash) fired power boilers. The systems are designed for injection of pulverized limestone into the boiler. Flue gases from the boilers flow to marble bed absorber-type scrubber modules installed in parallel and then to a steam heater designed to heat the gases to about 340 K.

The gases are scrubbed with recycled liquor and necessary makeup water. A purge stream is continually withdrawn to a settling system. Solids from this system are pumped to an unlined settling pond.

STATUS OF OPERATION

The decision to construct the two systems are made in late 1970. The first construction crews arrived on the site in September 1971, and the units were activated in September 1972. In March 1973, Unit No. 4 was modified to inject limestone at the inlet of the scrubber. As of June 1973, neither unit had performed according to design plans. Based on limited experience, SO_2 removal efficiencies exceeding 99 percent were indicated.

Process 3-5. Chalk to Scrubber Process[70]
Fulham and Tir John Power Stations
Great Britain

PROCESS DESIGN DESCRIPTION

The systems at the Fulham and the Tir John Power Stations were similar. Both systems were applied to coal fired power boilers and are now inactive.

Flue gases from the boiler flowed to a scrubber system and were discharged to the stack without reheat. The gases were scrubbed with a suspension of pulverized chalk (calcium carbonate) in recycled liquor and makeup water. A purge stream was withdrawn from the scrubber system and passed through a settling system before recycle. Solids from the settling system were filtered and dumped.

STATUS OF OPERATION

Both systems were installed about 1935 and 1936. The system at the Tir John Station never operated according to design plans and was finally abandoned. The system at the Fulham Power Station was brought on line according to design plans with the exception that maintenance costs were greater than anticipated. The Fulham system was shut down at the onset of World War II and was never reactivated. The system was reportedly highly efficient for removal of SO_2.

Process 3-6. Chalk to Scrubber Process[71]
Battersea Power Station
Central Electricity Generating Board
London, England

PROCESS DESIGN DESCRIPTION

The Battersea Power Station is equipped with two separate custom-designed emission control systems. System A serves eight coal-fired and one oil-fired power boiler associated with a combined rated power generating capacity of 243 Mw. System B serves six coal-fired power boilers associated with a combined rated generating capacity of 266 Mw. Flue gases flowing to System A are precleaned by 60- to 90-percent efficient cyclone arrestors; System B are precleaned by electrostatic precipitators with an efficiency on the order of 99 percent for grit and ash removal. Flue gases from the boilers connected to Systems A and B flow through separate but similar scrubber systems. Each of the systems is comprised of two, two-stage wooden lattice packed towers installed in parallel. Gases flow concurrent with the liquor in the first stage and countercurrent in the second state. Gases enter the towers at about 410 K and flow out of the stack at a discharge temperature of 290 to 300 K.

Thames River water is pumped to the first stage of the scrubbers. Chalk is added to the water pumped to the second stage. (The chalk used is a byproduct from a water softening process carried out by a nearby water treament company and purchased from them.) The liquor out of towers is split into two streams. The first-stage stream flows directly to a settling system; the second-stage stream is aerated prior to settling. Overflow from the settling system flows back to the Thames River. Solids removed from the settling system are dumped remote from the power plant site.

STATUS OF OPERATION

The scrubber systems were installed beginning in 1932. They were shut down during World War II because the plume would have been a landmark for bombers. System B has now been shut down for three years as part of an air quality experiment. Otherwise, both systems have operated according to design plans. Operating problems have included pump failures, sludge accumulation, and tower packing wear. However, unscheduled shutdowns are infrequent, with most of the corrective action being taken during an annual maintenance shutdown. The plant fires 1.0- to 1.5-percent sulfur coal and 2.5- to 3.0-percent residual fuel oil. The systems consistently reduce sulfur oxide concentrations from an inlet level of about 1 500 ppm to an outlet level ranging from 100 to 150 ppm.

Process 3-7. Chalk to Scrubber Process[72]

Bankside Power Station
Central Electricity Generating Board
London, England

PROCESS DESIGN DESCRIPTION

The Bankside Power Station is equipped with two flue gas washing systems installed in parallel which serve five oil-(2.5 to 3.5 percent sulfur) fired power boilers associated with a generating capacity of 300 Mw. Gases passing through the first stage of each washer are scrubbed countercurrently with spent power plant condenser cooling water to which limestone (chalk) slurry has been added. Gases pass downward through a second stage, then upward through a third stage where the gases are again scrubbed countercurrently with water and slurry. The first and third stages have wooden grid-type packing. Gases exit from the scrubbers to the stacks and are discharged at a temperature of about 290 K in the winter to about 310 K in the summer.

STATUS OF OPERATION

The first gas washer was activated in 1952. The systems operate according to design plans, consistently reducing SO_2 concentrations from inlet of about 1 600 ppm to outlet levels of about 50 ppm. The systems are shut down about twice each year for water nozzle cleaning, which takes 48 hours. The plant is shut down for four weeks each year for annual maintenance. Unscheduled shutdowns are rare.

Process 3-8. Limestone to Scrubber Process[67,73]
Will County Power Station
Commonwealth Edison Co.
Lockport Township, Illinois

PROCESS DESIGN DESCRIPTION

This process is retrofitted to handle the total flue gases from a 163-Mw pulverized coal (2.5 percent sulfur, 11 percent ash) fired power boiler.

Flue gases from the boiler flow to two scrubber systems installed in parallel. Each scrubber system is comprised of a venturi-type and plastic sphere-type scrubber installed in series. Gases leave the scrubber system at about 330 K and flow to a steam heater system designed to reheat the gases to about 370 K.

Scrubber liquor is recycled in a closed loop system which includes a settling system and an unlined settling pond. Pulverized limestone is added to the liquor entering the scrubber system. Solids are removed from the system and are stored in a lined basin prior to ultimate disposal.

STATUS OF OPERATION

Process selection activities were initiated in the spring of 1970, and engineering activities were begun in September 1970 prior to award of contract in November 1970. The first scrubber system was activated in February 1972, followed by the second system in April 1972.

As of November 1972, the system had not operated continuously according to design plans, runs being interrupted by a variety of problems including auxiliary equipment failures and blockage of flue gas flow. Under these conditions, sulfur oxide removal efficiencies ranged from 66 to 96 percent, and the concentration of particulate matter in the outlet gases ranged from 17 to 78 mg/m^3.

Process 3-9. Coral to Scrubber Process[67,68]
Key West Power Station
Key West Utility Board
Key West, Florida

PROCESS DESIGN DESCRIPTION

This system is designed to treat the flue gases from a new 37-Mw residual oil (2.8 percent sulfur) fired power boiler. Flue gases from the boiler flow to two inspirating-type scrubbers installed in parallel and are discharged without reheat.

Scrubber liquor is brackish well water fortified with pulverized coral. The scrubber liquor flows to an unlined settling pond which discharges to the ocean. It will eventually be necessary to dispose of solids from this pond.

STATUS OF OPERATION

The decision to install was made about February 1969, and a contract was awarded in April 1970. The system was activated in October 1972. As of June 1973, the system had not operated continuously according to design plans. Problems included carryover of solids from the scrubber and pulverizer malfunctions. The system is designed to remove 85 percent of the sulfur oxides and 95 percent of the particulate matter from the gas stream.

Process 3-10. Lime to Scrubber Process[67,68]
Sodersjukhuset Hospital
Stockholm, Sweden

PROCESS DESIGN DESCRIPTION

This process is designed to handle the total flue gases from three existing residual oil (2.5 percent sulfur) fired process boilers with a combines steam generating capacity equivalent to about 24.5 Mw. Each boiler is equipped with a separate baffle-type scrubber. Gases are exhausted from the boilers without reheat.

The gases are scrubbed with recycled liquor fortified with lime. Solids are removed from a settling system for disposal.

STATUS OF OPERATION

The systems have been operating since November 1969, consistently removing 97 to 98 percent of the sulfur oxides and about 90 to 95 percent of the particulate matter from the boiler flue gases.

Process 3-11. Carbide Sludge Lime to Scrubber Process[67,74,75]
Miike Power Station
Mitsui Aluminum Co.
Omuta City, Japan

PROCESS DESIGN DESCRIPTION

This process is designed to handle all of the flue gases from a new 156-Mw pulverized coal (2 percent sulfur) fired power boiler. Gases from the boiler flow to a 98-percent efficient electrostatic precipitator and then to two, two-stage venturi scrubber systems installed in parallel. Gases from the scrubbers flow to an oil-fired stack gas reheat system.

The gases are scrubbed with liquor recycled from an unlined settling pond and fortified with carbide sludge which analyzes about 85 to 90 percent calcium hydroxide. Solids from the system require disposal.

STATUS OF OPERATION

The project which resulted in the erection of the power station followed by installation of the scrubber system was begun in 1967. The project was approved in 1968, and construction of the power station was initiated in 1969. In 1970 the selection of the process was initiated followed by pilot-scale testing which was completed in March 1971; in the same month, the power generation system was activated. In June 1971, a purchase order was placed for the emission control system, and soon after, further pilot-plant tests were conducted. The emission control system was activated about April 1, 1972, and soon after, performed continuously according to design specifications. As of May 15, 1973, the scrubbers were still performing consistently according to design plans.

Although the system passed performance tests removing more than 90 percent of the sulfur oxides from the total gas flow at full capacity, the system is purposely operated to handle only 75 percent of the gas volume so as to only control emissions to the extent necessary to meet local air pollution control requirements. Under these conditions, SO_2 concentrations are reduced from inlet loadings of 1 900 ppm to outlet loadings of 180 ppm. Particulate matter outlet concentrations as low as 2.5 mg/Nm^3 have been reported.

Scrubber gases are reheated from a scrubber outlet temperature of 330 K to a reheat temperature of 350 K. The plant plans to convert the process from a sludge-type throwaway process to a process which will produce salable gypsum.

Process 3-12. Lime to Scrubber Process[75]
Amagasaki Power Station
Kansai Electric Power Co.
Osaka, Japan

PROCESS DESIGN DESCRIPTION

This process is designed to handle a portion of the flue gases from an existing 156-Mw power generation system. The two boiler units from which flue gases are withdrawn are residual oil (2.5 percent sulfur) fired power boilers.

The flue gases are precleaned by electrostatic precipitation and then pass to a two-stage plastic grid-type scrubber system. The gases are scrubbed with recycled liquor fortified with lime. A purge stream withdrawn from the recycle system is acidified and oxidized to produce gypsum which is centrifuged from the liquor to produce a salable product. There are no wastewaters from the system.

STATUS OF OPERATION

The system was activated in April 1972. Since then, the system has performed continuously according to design plans producing a salable gypsum product and removing 85 to 90 percent of the sulfur oxide from the flue gases treated.

Process 3-13. Thermal Regneration Sodium-Based Scrubber Process[75]
Chiba Plant
Japan Synthetic Rubber Co.
Ichihara City, Japan

PROCESS DESIGN DESCRIPTION

The system serves two residual oil (4 percent sulfur) fired steam boilers with a steam generating capacity equivalent to about 75 Mw. The system is comprised of two sieve-tray type absorption towers. Gases entering each tower are prescrubbed to remove particulate matter and are further scrubbed to remove sulfur oxides. The system is designed for reheat of the effluent gases by an oil-fired system.

The prescrubbing section of the towers is designed for water scrubbing. A purge stream withdrawn from this part of the tower is filtered and neutralized prior to discharge to the sewer. The sulfur oxides are removed by recycled liquor fortified with liquor from the regeneration system. A side stream is withdrawn from the scrubber liquor system for regeneration.

This stream is treated by thermal techniques to drive off SO_2 and to concentrate the stripped liquor. The SO_2 flows to a contact-type system which produces 98-percent sulfuric acid. Part of the treated liquor is returned to the scrubber liquor system and part is purged through the prescrubber liquor system being neutralized and filtered as previously described before discharge. About 10 percent of the sulfur removed from the gas stream is purged to the sewer in this manner.

STATUS OF OPERATION

Construction was initiated on this system in August 1971, and the system was activated in June 1972. As of November 1972, the system was operating continuously according to design plans, removing more than 90 percent of the sulfur oxides from the gas stream.

Process 3-14. Thermal Regneration Magnesium-Based Scrubber Process[67,76]
Mystic Power Station
Boston Edison Co.
Everette, Massachusetts

PROCESS DESIGN DESCRIPTION

The process is designed to treat the total flue gases from an existing 155-Mw residual oil (2.5 percent sulfur) fired power boiler. The regeneration system is located remote from the power plant site. The flue gases flow from the boiler to a venturi-type scrubber and then to the stack without reheat.

The gases are scrubbed with recycled liquor fortified with regenerated magnesium oxide. A side stream is withdrawn from the liquor system and is centrifuged to remove magnesium compounds. The centrifuge cake is dried and then shipped to the regeneration plant.

At the regeneration plant SO_2 is driven off the magnesium compounds by thermal techniques. The SO_2 flows to a system which produces 98 percent sulfuric acid. The stripped solids are returned to the power plant for reuse.

STATUS OF OPERATION

The decision to construct was made about June 1970, and the system was activated in April 1972. As of May 1973, the system had failed to perform continuously according to design expectations. Problems have included corrosion, erosion, and plugging and/or scaling in the liquid piping, centrifuging, conveying, and drying systems.

Process 3-15. Catalytic Oxidation Process [67]
Wood River Power Station
Illinois Power Co.
Wood River, Illinois

PROCESS DESIGN DESCRIPTION

The system is designed to treat all of the flue gases from an existing 100-Mw pulverized coal (3.1 percent sulfur, 10.7 percent ash) fired power boiler. Gases from the boiler are precleaned by a 99.6-percent efficient electrostatic precipitator and then flow to a system designed to convert the SO_2 to SO_3. The SO_3 is absorbed in a packed bed type tower which is connected to a mist elimination system. Gases exit at about 395 K.

The tower liquor is sulfuric acid which is produced at 77.7 percent concentration. There are no wastewaters from this system.

STATUS OF OPERATION

Design and capital cost estimates were initiated in June 1970, and detailed engineering and procurement were initiated in November 1970. On-site construction was begun in January 1971, and the high-efficiency electrostatic precipitator was placed in operation in January 1972 followed by activation of the entire system in September 1972. As of June 1973, the system has not operated continuously according to design plans. Operations have been seriously hampered by the lack of sufficient natural gas to preheat the gases prior to catalytic oxidation. This has necessitated extensive modifications to accommodate oil firing in lieu of gas firing. These modifications are not yet complete.

Process 3-16. Activated Carbon Process [75]
Sakai Power Station
Kansai Electric Power Co.
Osaka, Japan

PROCESS DESIGN DESCRIPTION

This process is designed to treat 150 000 actual cubic feet per minute of a side stream from an existing residual oil (2 percent sulfur*) fired boiler. Flue gases pass through a mechanical collector into a spray-type cooler and then into two moving bed-type activated carbon adsorbers installed in parallel. The rich carbon from the adsorbers is continuously removed and desorbed in a moving bed type tower. Desorbtion is accomplished by carbon contact with recycled inert gas (620 K) formed by controlled combustion of butane. Lean carbon is returned to the adsorption towers. A purge stream is withdrawn from the sweep gas at controlled SO_2 concentrations ranging from 10 to 20 percent.

The purge stream is cleaned by mechanical separation and then processed in a contact-type process which produces 98 percent sulfuric acid. The tail gas from the sulfuric acid process is returned to the spray-type gas cooler. Water from the gas cooler is discharged to the sewer.

STATUS OF OPERATION

The system was activated in February 1972. As of August 1972, the system was continuously and consistently removing from 80 to 95 percent of the SO_2 from the flue gases. Operating costs have been reportedly much higher than those for other types of gas desulfurization processes operating in Japan.

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*Actually 0.75 percent sulfur oil is being used.

Process 3-17. Activated Carbon Process[75]
Kashima Power Station
Tokyo Electric Co.
Kashima, Japan

PROCESS DESIGN DESCRIPTION

The process is designed to treat one fourth of the flue gases from an existing 600-Mw residual oil (1.6 percent sulfur) fired power boiler. Gases from the boiler flow to electrostatic precipitators designed to reduce particulate matter concentrations to 0.02 grains per standard cubic foot and then to the activated carbon adsorbers. The activated carbon adsorbers are designed to operate on a 63-hour cycle: washing 7 hours, drying and adsorption 20 hours, and adsorption 36 hours. The adsorbed SO_2 oxidizes in place to SO_3 and is water washed from the activated carbon to produce 20-percent sulfuric acid. This acid is neutralized with pulverized limestone, and the gypsum produced is centrifuged from the slurry. Liquid from the centrifuges is discharged to the sewer.

STATUS OF OPERATION

The system was activated in March 1971. As of August 1972, the system was continuously, consistently removing about 80 percent of the sulfur oxides from the gas stream treated. Operating costs have been reportedly much higher than those for other types of gas desulfurization process operating in Japan.

Process 3-18. Water Scrubbing Process[67]
Valmont Power Station
Public Service Company of Colorado
Boulder, Colorado

PROCESS DESIGN DESCRIPTION

Although this process is designed primarily for removal of particulate matter, some sulfur oxides are incidentally removed. The process is designed to treat about 60 percent of the flue gases from an existing 165-Mw pulverized coal (0.5 percent sulfur, 7 percent ash) fired power boiler. About 60 percent of the flue gases from the boiler pass through a mechanical collector and then into two, three-stage plastic sphere-type scrubbing systems installed in parallel. Gases from the scrubbers are reheated prior to being mixed with the remainder of the flue gases.

Scrubber liquor is recirculated water from which a side stream is withdrawn to an unlined settling pond.

STATUS OF OPERATION

The system was activated in November 1971. As of June 1973, outlet particulate matter concentrations were less than 46 mg/m^3 and sulfur oxide removal efficiences were about 45 percent, with operations hampered by a need for shutdown for cleaning about every 30 days.

Process 3-19. Water Scrubber Process[67]
Cherokee Power Station
Public Service Company of Colorado
Denver, Colorado

PROCESS DESIGN DESCRIPTION The purpose and design of this system is similar to that described in Process 3-18. The system is designed to treat all of the flue gases from an existing 150-Mw pulverized coal (0.55 percent sulfur, 9 percent ash) fired power boiler.

STATUS OF OPERATION The system was activated in February 1973 and as of June 1973 had operated on a substantially continuous basis since March 23, 1973, removing about 20 percent of the sulfur oxides and reducing outlet particulate matter concentrations to about 46 mg/m^3.

water discharges when operated open loop or may involve seepage into ground waters when operated closed loop with unsealed settling ponds. Solids from these systems require disposal.

3.4.1.10 Fluidized Bed Combustion with Limestone Treatment--In fluidized-bed combustion, fuel is burned in a fluidized bed of noncombustible solids which provide for improved transfer of heat to the wall of the combustion chamber. Heat transfer coefficients are 3 to 10 times greater than those in a conventional boiler; thus the heat transfer surface can be reduced, and relatively low temperatures can be maintained in the combustion zone. Low superficial velocities, 0.6 to 4 m/s in conventional boiler furnaces, must be utilized to avoid blowing out the bed.[66]

Because of the intimate gas-solids contacting, fluidized beds offer promise for reducing both SO_x and NO_x emissions. With fluidized limestone-dolomite sorbent, 90- to 95- percent reduction of SO_2 has been achieved.[65] Since nitrogen oxide formation is inhibited by the low bed temperature, NO_x concentrations have been reportedly reduced in pressurized systems to 50 to 150 ppm.[67] Other results indicate reductions in atmospheric systems to 325 to 370 ppm.[67]

Fluidized-bed combustion systems have been studied above atmospheric pressure as well as at 101 kN/m^2. Pressurized fluidized-bed combustion at 354 to 505 kN/m^2 with dolomite can possibly remove 80 to 90 percent of SO_x;[68] uncalcined limestone results in 66- to 85-percent removals.[67] No deposits or erosion problems were found during the test program.[67] A different system with a capacity of 0.1 kg per second of coal has been operated at 505 kN/m^2.[68]

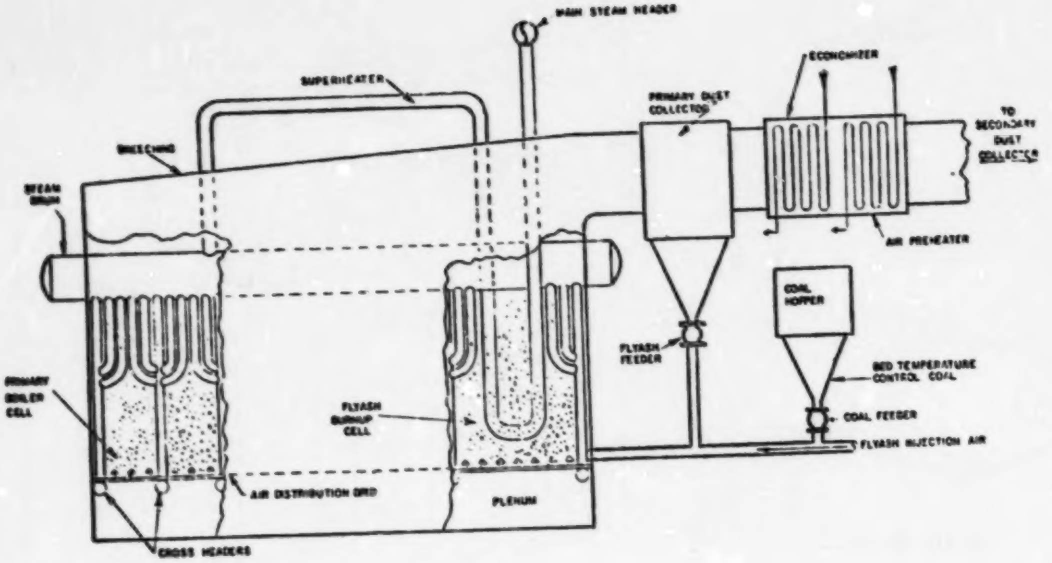
Atmospheric pressure fluidized-bed combustion systems have been under development both in this country and abroad. A number of conceptual designs based on long-term laboratory and pilot tests have been provided.[69] Design studies have been made for 120-MW and 660-MW, coal-fired, fluidized-bed combustion systems;[70] and a coal-fired boiler producing 5 kg per second of steam is being developed to compete with oil-fired units.[71] Also, a unit producing 22 kg per second of steam has been designed for installation at Grimethorpe (England).[70]

A 25 kg/s fluidized-bed combustion boiler for industrial use[68] (Figure 3-18) might consist of several 0.46- by 0.31 m fluidized-bed combustion modules with a carbon burnup cell and with sulfur dioxide emissions controlled by dry limestone injection.

The Ignifluid boiler (Figure 3-19), commercially available in France, incorporates some features of atmospheric fluidized-bed combustion. Fluidization of coarse feed coal takes place on a moving inclined grate. The bed temperature (between 800 and 920 K) causes coal ash to agglomerate, expand, and sink through the bed to the grate. However, no heat transfer surface is placed in the bed, and the use of limestone or dolomite for SO_x control has not been practiced. A 60-MW Ignifluid boiler has been built, and a 257-MW unit is being evaluated for construction in the United States.[72]

Combined-cycle systems--Combined-cycle systems fire fuel in gas turbines to generate electrical energy and utilize the thermal energy of the turbine exhaust to generate steam. The steam is used in steam turbines to generate additional electrical energy or to provide heat for other processes, thereby increasing efficiency as discussed in Section 3.2.

Several conceptual designs of pressurized fluidized-bed combustion, combined-cycle utility boilers have also been studies.[68] In one such system (Figure 3-20), air and crushed dried coal are fed to a fluidized bed of dolomite, which is regenerated and recycled. Sulfur is removed in the fluidized bed, then released in the sorbent regeneration process, and converted to sulfur in a subsequent recovery process (Section 2.2.2). Bed temperature is maintained below the agglomeration point by efficient heat transfer to the boiler surface. Ash from the coal, together with unburned carbon and


MAIN STEAM HEADER
SUPERHEATER
BREECHING
STEAM DRUM
PRIMARY DUST COLLECTOR
ECONOMIZER
TO SECONDARY DUST COLLECTOR
AIR PREHEATER
COAL HOPPER
FLYASH FEEDER
BED TEMPERATURE CONTROL COAL
COAL FEEDER
FLYASH INJECTION AIR
PRIMARY BOILER CELL
FLYASH BURNUP CELL
AIR DISTRIBUTION GRID
PLENUM
CROSS HEADERS

Overall dimensions : 3.7 m wide by 4.9 m high by 12.2 m long

Fig. 3-18. Schematic fluidized-bed boiler incorporating a carbon burn-up cell.

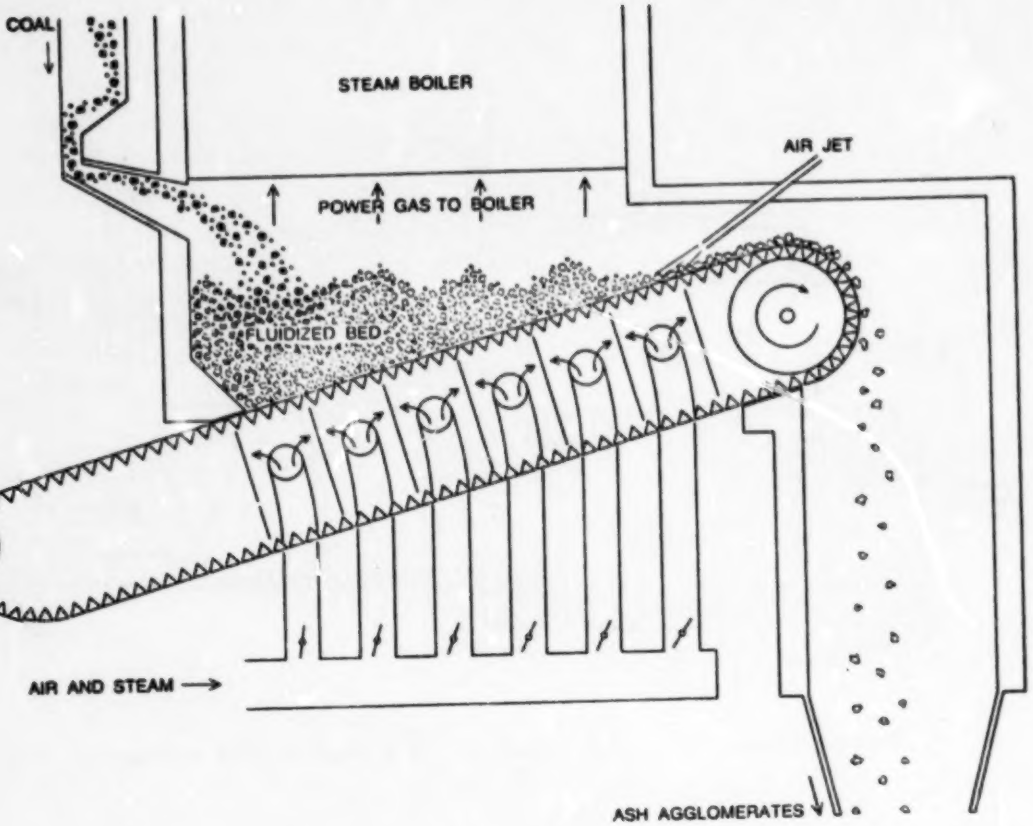
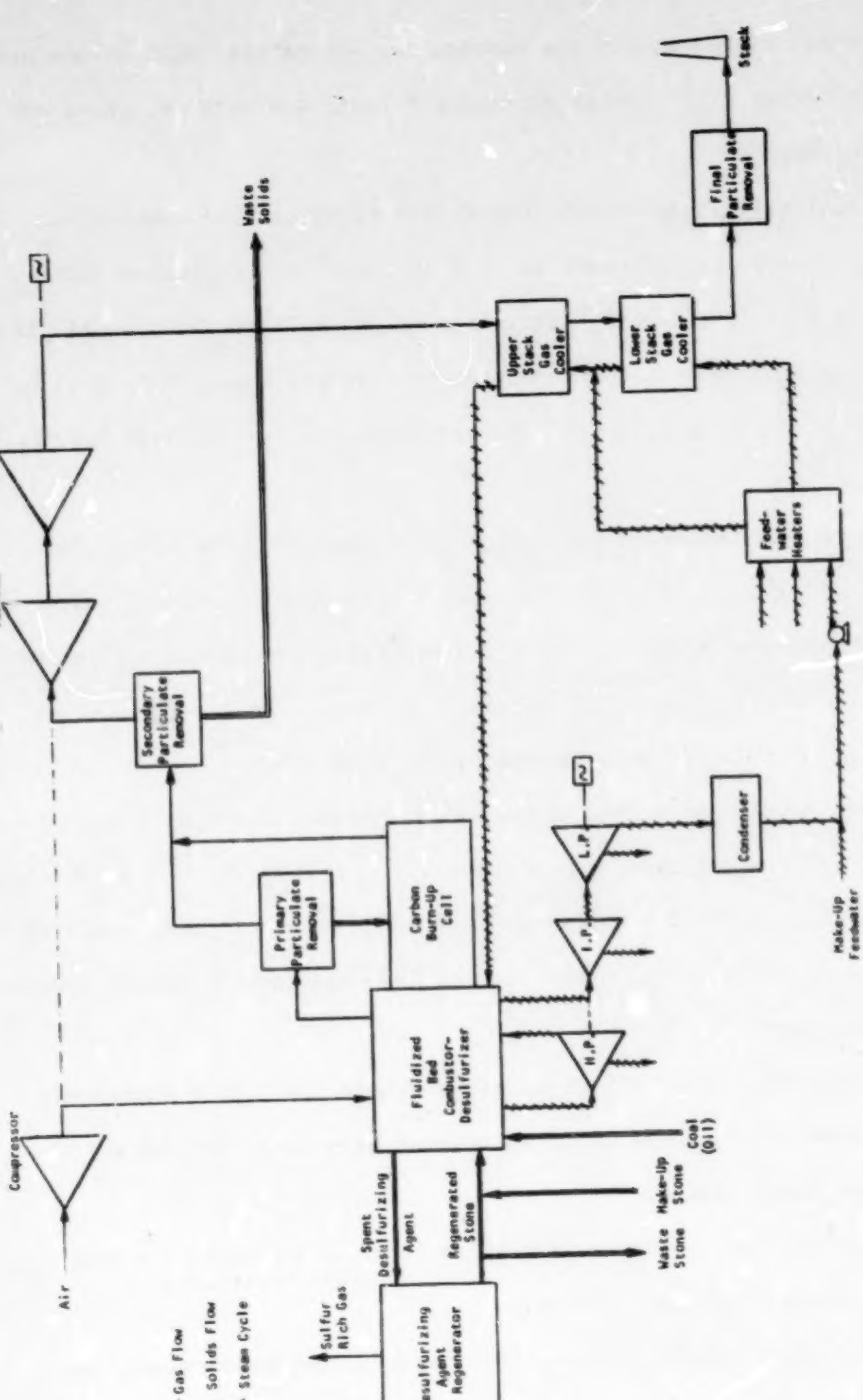

COAL
STEAM BOILER
AIR JET
POWER GAS TO BOILER
FLUIDIZED BED
AIR AND STEAM
ASH AGGLOMERATES

Fig. 3-19. Ignifluid boiler combustion section



Gas Flow
Solids Flow
Steam Cycle
Air
Compressor
Compressor Turbine
Power Turbine
~
Waste Solids
Stack
Final Particulate Removal
Upper Stack Gas Cooler
Lower Stack Gas Cooler
Feed-water Heaters
Secondary Particulate Removal
Primary Particulate Removal
Carbon Burn-Up Cell
Fluidized Bed Combustor-Desulfurizer
Desulfurizing Agent Regenerator
Sulfur Rich Gas
Spent Desulfurizing Agent
Regenerated Stone
Waste Stone
Make-Up Stone
Coal (Oil)
H.P.
I.P.
L.P.
~
Condenser
Make-Up Feedwater

Fig. 3-20. Pressurized fluid bed boiler system.

attrited sorbent, is removed in the particulate separators, with carbon being burned in the burnup cell. After expansion through the turbine, gases are cooled and released.

The overall efficiency of this conceptual fluidized-bed combustion, combined-cycle system is estimated at 38.4 percent;[66] the estimated full-load heat rate is 9.2 MJ/kw-hr.[66] Estimated emissions from the overall plant, including the sulfur removal and regeneration systems, are 0.39 to 0.43 μg of SO_2 per Joule, 0.03 to 0.1 μg of NO_x per Joule Btu, and 0.01 to 0.07 μg of particulates per Joule.

The pressurized fluidized-bed combustion, combined-cycle system for coal has not been demonstrated at full scale. Conceptual designs, costs, and schedules for a 10- to 30-MW development plant have been made. A proposed schedule calls for construction of such a plant during 1973, with testing through 1977 to be followed by a demonstration after 1979.[73]

Analytical studies have been conducted of various fluidized-bed combustion, combined-cycle configurations at pressure ratios up to 15:1 at 700 K. An analytical comparison of pressurized fluidized-bed combustion, combined-cycle plants with conventional power plants, both system equipped to remove SO_2, concluded that--

1. the capital cost of a pressurized combined cycle with fluidized-bed combustion may be 18 to 21 percent less than that for a conventional system,
2. the energy cost could be as much as 10 to 12 percent less than that for conventional plants,
3. pressurized combined-cycle, fluidized-bed combustion plants may be more effective for reducing SO_x emissions than conventional plants, and
4. pressurized combined-cycle, fluidized-bed combustion plants may have greater overall plant efficiency than conventional plants.

Coal gasification has also been studied in conjunction with fluidized-bed, combined-cycle systems. The use of pressurized fluidized-bed gasification systems to produce a low-heat content, low-sulfur gas for a combined-cycle power plant has been proposed[74] (Figure 3-43). The gasifier produces a low heat content pressurized gas (4.7 to 9.4 MJ/m^3), which is fired in a combustor turbine. The residual energy in the expanded flue gas is captured in a heat recovery boiler, into which supplementary fuel is fired to obtain superheated steam.

Many of the conventional gasification schemes proposed or under development for producing high-heat content pipeline gas (Section 3.3.1.4) might be modified to produce low-Btu gas under pressure. These systems include the Lurgi, the CO_2 Acceptor, the Hygas, Bygas, and Synthane processes. Another project involves development of a coal-gasification scheme compatible with a 10-atmosphere, combustor-turbine system. Sulfur removal in the fluidized-bed gasifiers using dolomite or lime has been proposed.

3.4.2 Other Combustion Process Waste Gas Desulfurization Activities

3.4.2.1 Other Development Activities in the United States -- A number of additional systems are at various stages of application; some are being offered for commercial demonstrations and others are in earlier stages of development. Those being offered for demonstration include char sorption systems by Foster-Wheeler and Commonwealth Associates, sodium solution scrubbing systems with electrolytic regeneration by Stone and Webster, and Ionics, and a dry sorption system by Esso Research and Engineering and by Babcock & Wilcox. These three systems are discussed individually in Sections 3.4.3.2 through 3.4.3.4; those systems in earlier stages of development are discussed in Section 3.4.2.4.

Char sorption processes[75]--In char sorption processes, SO_2 is absorbed on char, catalyzed to SO_3, and then hydrolyzed to sulfuric acid on the char sur-

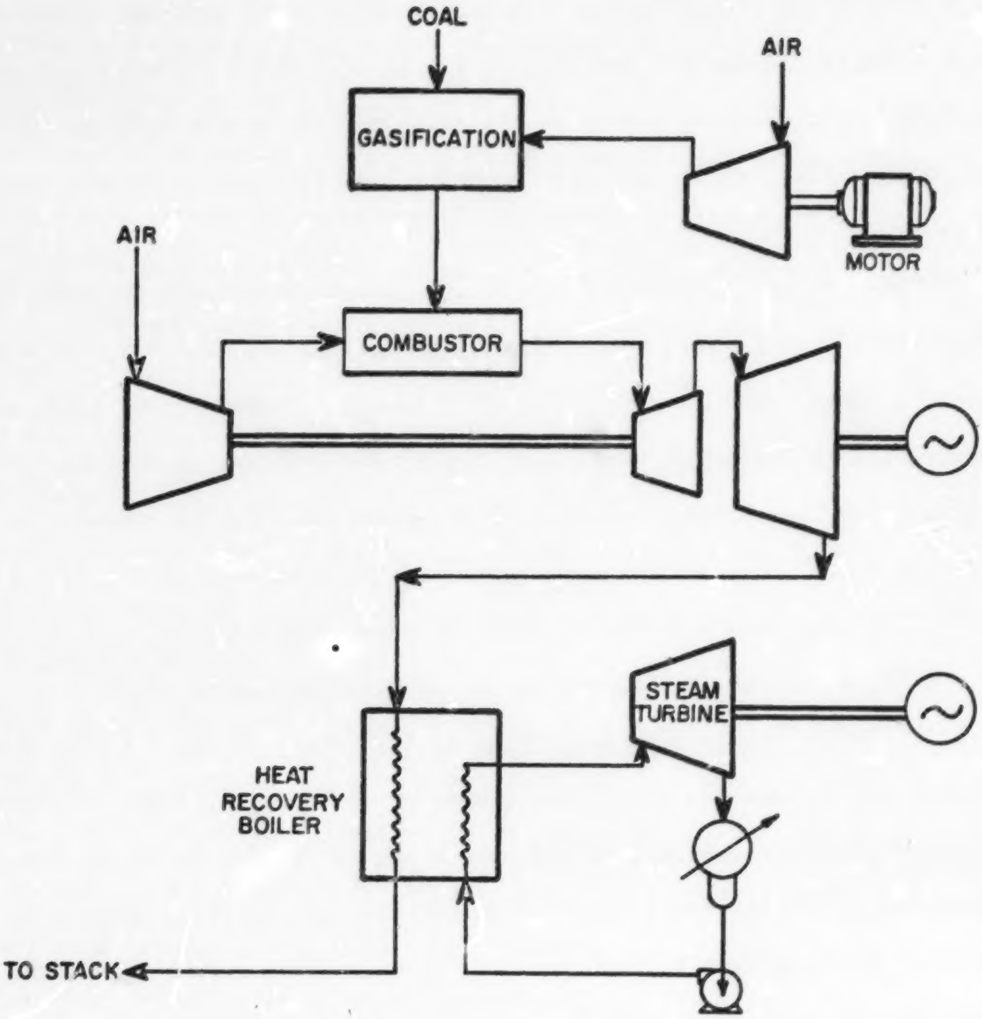

COAL
AIR
GASIFICATION
MOTOR
AIR
COMBUSTOR
STEAM TURBINE
HEAT RECOVERY BOILER
TO STACK

Figure 3-21. Coal gasification, combined-cycle system.

face. Because effectiveness depends on the presence of oxygen and water, the process is primarily applicable to treatment of effluent gases (e.g., combustion products) which have both present. Char sorption is favored by low temperatures, but 420 to 450 K is a satisfactory range. Thus it is possible to reject cleaned gases at temperatures giving sufficient plume buoyancy to eliminate the need to reheat. Available processes differ in mechanical details but usually use either thermal regeneration or water washing to remove sulfuric acid. Two U.S. companies, Commonwealth Associates and Foster-Wheeler, are offering char sorption systems. Both are thermally regenerable processes developed in Germany and licensed for sale in the United States.

Process description -- Thermally regenerable systems heat the acid-laden char either with inert gas (Commonwealth Associates) or with hot sand in an inert atmosphere (Foster-Wheeler). At about 670 K the sulfuric acid reacts with the char to produce SO_2, carbon dioxide, and water. Regeneration gradually degrades char by increasing the pore size; therefore, it is necessary to remove fines and to add fresh carbon as makeup. The process is not sensitive to contamination by fly ash, which is removed along with fine char by screening. Concentrated SO_2, suitable for conversion to sulfuric acid, is produced.

Development history -- Thermally regenerable processes in the United States are products of pilot plant developments in Germany and design studies conducted by U.S. licensees. The Commonwealth Associates process is based on the Reinluft process investigated on several pilot systems between 1959 and 1968. The process is considered by its developers to be ready for installation on a 300-Mw power boiler. The Foster-Wheeler process is based on work by Bergbau-Forschung, the coal industry laboratory in Germany. Opportunities to demonstrate the process on a 30- to 100-Mw system are being sought.

Sodium solution scrubbing-electrolytic regeneration[76,77]--The Ionics Corporation has teamed with Stone and Webster to develop a system which combines sodium scrubbing advantages with an electrolytic regeneration that produces no waste.

Process description -- The process consists of three basic steps: 1) reaction of the SO_x with a sodium hydroxide solution, 2) neutralization of the resulting sodium sulfite-bisulfite solution with sulfuric acid to release SO_2 and produce a sodium sulfate solution, and 3) electrolytic conversion of the sodium sulfate solution to sodium hydroxide for recycle and sulfuric acid for neutralization. The process produces high purity SO_2 and sulfuric acid. It can be designed to produce no waste if dilute sulfuric acid can be used; if sulfuric acid is not usable, either sulfate removal or neutralization of the acid is necessary.

Development history -- The process incorporates well-established sodium scrubbing technology. Electrolytic cell technology is also well developed but must be extended to a new application and a larger scale of operation. Development of an integrated system was started with pilot plant work at Gannon Station of Tampa Electric in 1968-1969 and has been supplemented with studies on the scale-up of the electrolytic cell. Although the process has been offered for commercial demonstration, full-scale trials have been scheduled; however, the Enviromental Protection Agency and Wisconsin Electric Power Company have contracted to demonstrate a 75-Mw plant after successful completion of a 15-month, Phase I pilot-plant study.

Absorption on reactive solids--reducing gas generation (Esso/B&W) [78] -- Esso Research & Engineering and Babcock & Wilcox have teamed to develop and offer a proprietory process for demonstration on a 100-Mw power boiler.

Process description -- Process details have not been released. The process is said to collect SO_x on a solid adsorbent material which is contacted with the gas stream. It is also said that the sorbent material can be regenerated to produce either sulfur of sulfuric acid.

Development history -- Program development since 1968 has included pilot plant trials of both sorption and regeneration and has been supported by 17 utility companies in the United States and Canada. This process will be piloted at the Tanners Creek power plant of the Indiana and Michigan Electric Company with construction set for completion by late 1974.[79]

Other Processes in Development in the United States processes have not reached the point of being offered for full-scale applications. At present, 12 such processes are being studied; most of these have been under development for some time. Few new approaches have been suggested in recent months since flue gas cleaning systems that are either in advanced developmental stages or have already been offered commercially will probably meet national needs for add-on equipment.

Processes and developers - North American Rockwell is developing a molten carbonate scrubbing system which reacts a eutectic mixture of sodium, lithium, and potassium carbonates at 720 K with SO_x in flue gases.[80] The process, combining the rapid mass transfer of liquid scrubbing with the rapid chemical reactions of high temperature operation, is to be tested on a pilot plant of 10-Mw equivalent on an oil-fired boiler at the Arthur Kill Station of Consolidated Edison. The scrubbing liquid regenerated in a two-step process produces hydrogen sulfide, which can be processed to produce elemental sulfur.

Dry injection of limestones and dolomites is being studied by the Environmental Protection Agency in cooperation with the Tennessee Valley Authority and by Foster-Wheeler. Removal efficiencies with full-scale boilers of about 23 percent (even with twice stoichiometric quantities of reactant) have been disappointing in the EPA-TVA trials, but recent results from the Foster-Wheeler work indicate that 50-percent efficiency is attainable using high-calcium lime.

The Consolidation Coal Company has developed and is testing, along with the Philadelphia Electric Company, a potassium formate scrubbing system.[81] A concentrated (85 percent) aqueous solution of formate is used to scrub SO_2, and a two-step process is used to regenerate the absorbent and produce hydrogen sulfide. The process offers the advantage of sulfate reduction, which occurs as part of the regular regeneration steps.

Since 1968, the Bureau of Mines has investigated a sodium citrate scrubbing process that produces byproduct sulfur.[82] The process was tested for control of primary smelters at Magma Cooper in San Manuel, Arizona; a demonstration is under consideration; and the process is also a candidate for cleaning of combustion gases. A 0.95 Nm^3/s pilot plant will be designed and installed by Arthur G. McKee and Peabody Engineering on a coal-fired boiler at the Terra Haute, Indiana plant of Pfizer, Incorporated. In addition to the McKee and Peabody citrate work, the Bureau of Mines in presently constructing a small citrate pilot plant to treat flue gas from an oil-fired furnace of the Bureau's Pittsburgh Energy Research Center. Startup is expected in January 1973.

Ammonia scrubbing of stack gases with ammonium sulfite and bisulfite is being studied in field pilot-scale trials by the Environmental Protection Agency and Tennessee Valley Authority.[83] The Scrubbing liquor is acidified with ammonium bisulfate to evolve SO_2 and form ammonium sulfate, which is decomposed into ammonium bisulfate and ammonia for recycle. Monsanto recently announced that they are also researching an ammonia scrubbing system which incorporates thermal decomposition of the ammonium reaction products to produce SO_2, nitrogen, and water. The SO_2 is converted to sulfuric acid or sulfur.

A char sorption system which incorporates reducing gas regeneration is being developed by Westvaco with the support of the Environmental Protection Agency.[84] The char, loaded with sulfuric acid, is contacted with hydrogen sulfide to produce sulfur, which is stripped off with steam. The process has been studied since 1968 on a small scale.

U.O.P. is working to develop a proprietary aqueous process which produces sulfur as a byproduct. The process is being studied in cooperation with Commonwealth Edison on a 30-Mw pilot plant.

Organic absorbents in aqueous solutions are being studied by Monsanto.[85] Two systems, one with lime regeneration and another with thermal regeneration, are said to be under development. The lime regenerable system will be pilot tested on a 0.95 Nm^3/s system at the Elmer W. Stout Station of Indianapolis Power and Light Company.

3.4.2.2 Other Activities Outside the United States

SO_2 removal processes in the BRD--In the BRD, four dry processes for SO_2 removal have been critically examined:

1. Additiv Verfahren (Wickert)
2. Reinluft-Verfahren
3. Stillverfahren
4. Bergbau-Forschungs-Verfahren.

A description of these processes is presented in Table 3-14.[86,87]

Three processes using wet cleaning approved in the BRD are:

1. Bischoff-Verfahren
2. Lurgi-Sulfacid-Verfahren
3. Grillo-AGS-Verfahren

   [Bergbau-Forschung (wet regeneration)].

Table 3-15 gives a characterization of the processes and shows their application or the present state of development.[86,87]

Table 3-14. - SO_2 REMOVAL PROCESSES, DRY BASIS, BRD[86,87]

Process	Description	Present state of development/ application	Efficiency, percent	Byproduct
Bergbau-Forschung	Dry adsorption on moving bed or activated coke, hot gas desorption.	1.1 Nm^3/s proved; 42 Nm^3/s planned	90	SO_2
Reinluft	Adsorption on lignite coke; hot gas desorption.	9.2 Nm^3/s; experiments finished	65 - 75	SO_2
Additiv	Pulverized limestone injection.	Experiments finished	20 - 40	waste
Still	Adsorption on wet filter from lignite ash (CaO).	$6.9(10^{-3}) Nm^3/s$; experiments finished	90	waste

Table 3-15. - SO_2 REMOVAL PROCESSES, WET BASIS, BRD[86,87]

Process	Description	Present state of development/ application	Efficiency, percent	Byproduct
Bischoff	Wet lime scrubbing.	0.04 Nm^3/s; under test	80 - 90	$CaSO_4$ or waste
Lurgi-Sulfacid	Gas adsorption on coal in fixed bed; desorption with water.	$8.3(10^{-3})$ Nm^3/s; commercialized	90	H_2SO_4 diluted
Grillo AGS	Manganese oxide and magnesium oxide; regeneration by roasting.	$7.5(10^{-3})$ Nm^3/s; experiments finished. $2.8(10^{-2})$ - 56 Nm^3/s planned.	90	H_2SO_4 or SO_2

Japan -- In Japan work has progressed to semicommercial scale on two government supported projects--the Mitsuhishi Manganese Oxide process and the Hitachi Char process. The latest versions being installed on power boilers have capacities of 92 and 117 Nm^3/s. The Shell process, developed in the Netherlands, involves absorption with cupric oxide on alumina; it is being installed on an oil-fired boiler emitting 33.4 Nm^3/s. The Grillo process, developed in Germany, also involves sorption on metal oxides; it is being studied on pilot scale. Five companies have reported different varieties of magnesium oxide sorption. A number of other systems are the subjects of small-scale investigations.

France -- Studies of ammonia scrubbing by Ugine Kuhlman, Weirtam, and Electricite de France are based on a double alkali system in which the scrubbing liquor is regenerated with lime to produce a waste sludge. Also under study is a thermally regenerable system. The Institute Francaise du Petrole (IFP) is developing an ammonia scrubbing system in which the scrubbing liquor is evaporated to ammonia, SO_2, and water; a Claus unit produces sulfur and ammonia for recycle.

Other development—Other developments are in eastern European countries. In the USSR, a magnesium scrubbing system is reported to be the most promising. In Romania, a number of systems which appear to be highly specific are being investigated. In Poland, work is underway on injection of ammonia and limestone for reaction in the gas stream. In Czechoslovakia, ammonia scrubbing, recently recommended for scale-up, has not been approved, and the only current work involves limestone injection.

REFERENCES FOR CHAPTER 3

1. Weaver, Kenneth F. "The Search for Tomorrow's Power," National Geographic 142(5):662-663.

2. Oil and Gas Journal, July 31, 1972.

3. "Study of the Future Supply of Low Sulfur Oil for Electrical Utilities," Office of Air Programs, EPA, Contract No. EHSD 71-43, HIT-499, February 1972.

4. Linden, Henry R. "The Outlook for Synthetic Fuels," presented at the Second Annual Meeting of the Division of Production, American Petroleum Institute, Dallas, Texas, March 6-8, 1972.

5. "Summary of Natural Gas Reserves for Year 1966." Report of the Committee on Natural Gas Reserves of the American Gas Association, March 1967.

6. Minerals Yearbook. Department of the Interior, Bureau of Mines, 1970.

7. U. S. Energy Outlook: An Initial Appraisal, 1971-1985, Vol. 1, Interim Report, National Petroleum Council, Committee on U. S. Energy Outlook, July 15, 1971.

8. Sullivan, F. P. "Oil from Canadian Tar Sands Begins Its Flow to Market," Power, 3(12):77-80, December 1967.

9. "Status of Central Station Nuclear Power Reactors." Atomic Energy Commission, WASH-1208, December 1972.

10. "The National Power Survey." Federal Power Commission, December 1971.

11. "Nuclear Power and Uranium." Remarks by J. A. Patterson, Atomic Energy Commission, before the Gulf Association of Geological Societies, October 13, 1972.

12. "American Power Conference Abstracts." Combustion, 39(2):19-29, August 1967.

13. Gourdine, M. "Electrogasdynamics, or EGD for Short." Combustion, 39(7): 13-16, January 1968.

14. Gourdine, M. "Electrogasdynamics and the Coal Industry." Preprint. (Presented at the National Coal Association Technical Sales Conference, Annual Meeting, Pittsburgh, Pennsylvania, September 15, 1966).

15. Letter E.J. Willson, Jr., United Aircraft Corp. to John O. Copeland, Research Triangle Park, N.C., June 5, 1973.

16. A.B. Crouchley and C.E. Caroll, The Design and Economics of On-Site Generation with Aircraft-Type Gas Turbines for a Chemical Complex, presented at ASME Conference, Houston, Texas, January 3, 1967.

17. F.R. Jackson, "Repowering with Combined Cycle Solves Utility Power Needs", Diesel and Gas Turbine Progress, August 1971.

18. A Deurbrock, et al. "Physical Desulfurization of Coal." 1972 AIChE Meeting, Paper No. D28.

19. An Evaluation of Coal Cleaning Processes and Techniques for Removing Pyritic Sulfur from Fine Coal (Final Reports). Contract Nos. Ph-86 67-139 and CPA 70-26.

20. Sulfur Reduction Potential of the Coals of the United States. U. S. Bureau of Mines, RI 7633 (1972).

21. "Economics of a Process to Produce Ashless, Low-Sulfur Fuel from Coal." Pittsburgh and Midway Coal Mining Company. R&D Report No. 53, Interim Report No. 1, prepared for Office of Coal Research (June 1970).

22. "Summary Report on Project Gasoline." Consolidation Coal Company. R&D Report No. 39, Vol. 1, prepared for Office of Coal Research (April 1970).

23. "Char Oil Energy Development." FMC Corporation. R&D Report No. 56, Interim Report No. 1, prepared for Office of Coal Research (May 1970).

24. J. F. Farnsworth and R. A. Glenn. "Status and Design Characteristics of the BCF/OCR Bi-Gas Plant." Am. Chem. Soc., Div. Fuel Chem., Preprint 15(3):12-31 (1971).

25. Control Techniques for Sulfur Oxide Air Pollutants (Second Ed. Draft). U. S. Environmental Protection Agency (November 20, 1972).

26. H. C. Hottell and J. B. Howard. New Energy Technology--Some Facts and Assessments. Massachusetts Institute of Technology (October 1972).

27. "Coal-to-Gas Pilot Plant." Mines Magazine, 62(10):4-6, 8, 10 (October 1972).

28. R. J. Grace, R. A. Glenn, and R. L. Zahradnik. "Gasification of Lignite by BCR Two-State Super-Pressure Process." Ind. Eng. Chem. Process Design Develop., 11 (1);95-102 (1972).

29. A. J. Forney, W. P. Haynes, J. J. Elliott, and R. F. Kenny. Clean Automotive Fuel: Laboratory-Scale Operation of the Synthane Process.

30. G. T. Skaperdas. Commercial Potential for the Kellogg Coal Gasification Process (Final Report). M. W. Kellogg Co., Piscataway, J. J., OCR Contract No. 14-01-0001-380, R&D Report No. 38 (September 1967).

31. A. E. Cover, W. C. Schreiner, and G. T. Skaperdas. "The Kellogg Coal Gasification Process." Am. Chem. Soc., Div. Fuel Chem., Preprint 15 (3): 1-11 (September 1971).

32. F. L. Robson, et al. Technological and Economic Feasibility of Advanced Power Cycles and Methods of Producing Nonpolluting Fuels for Utility Power Systems. United Aircraft Research Laboratories, prepared for National Air Pollution Control Administration (December 1970).

33. "Routes to Low Sulfur Fuel Oil." Industrial Petroleum, 40 (June 1972) and Oil & Gas Journal (September 11, 1972).

34. Private information from MWV Hamburg.

35. Oil & Gas Journal, July 17, 1972.

36. Chemical Economy and Engineering Review, 2(5):19-21 (May 1970).

37. R. N. Shreve. Chemical Process Industries (3rd ed.). McGraw Hill (1967).

38. 1970 Refinery Process Handbook. Hydrocarbon Processing (September 1970).

39. Environmental Portection Agency, Unpublished data.

40. J. B. Hyne. "Methods for Desulfurization of Effluent Gas Streams." Oil and Gas Journal, August 28, 1972, pp. 64-78.

41. R. J. Hengstebeck. Petroleum Processing Principles and Applications. McGraw-Hill (1959).

42. L. S. Reid. "Desulfurization Processes for Natural Gas Liquids." Proceedings of 49th Annual Convention, Natural Gas Processors Association. Denver, Col., March 17-19 1970, pp. 104-108.

43. J. W. Palm. "Sulfur Plant Design." Hydrocarbon Processing, March 1972, pp. 105-108.

44. B. W. Gamson and R. H. Elkins. "Sulfur from Hydrogen Sulfide." Chemical Engineering Progress, 49(4):203-214 (1953).

45. F. S. Mallette. Problems and Control of Air Pollution. Reinhold (New York) (1955).

46. A. R. Valdes. "New Look at Sulfur Plants." Hydrocarbon Processing, 43(3):104-108 (March 1964) and 43(4):122-128 (April 1964).

47. M. J. Carmassi and J. P. Zwindling. "How SNPA Optimizes Sulfur Plants." Hydrocarbon Processing, 46(4):117-121 (April 1967).

48. B. B. Barry. "Reduce Claus Sulfur Emissions." Hydrocarbon Processing, April 1972, pp. 102-106.

49. J. B. Hyne. "Methods for Desulfurization of Effluent Gas Streams." Oil and Gas Journal, August 28, 1972, p. 64.

50. G. E. Mitchell. "Environmental Protection—Benicia Refinery." Proceedings, 1970 Mid-Year Meeting of American Petroleum Institute Division of Refining, May 13-15, 1970.

51. L. L. Laster. "Air Pollution Aspects of the Petroleum Refinery Industry." Memorandum, Control Systems Division, EPA (December 1971).

52. "Tail Gas Desulfurization Operations Successful." Oil and Gas Journal, February 7, 1972, p. 65.

53. "The Beavon Sulfur Removal Process for the Purification of Sulfur Plant Tail Gas." Ralph M. Parson Co. Bulletin.

54. "Clean Air" and "Sulfur Recovery by the Stretford Process." Pritchard Co. Bulletins.

55. G. L. Thomas and E. Plum. "Sulfur Recovery by the Clean Air Sulfur Process." National Meeting of AIChE, Dallas, Texas, February 1072.

56. A. B. Coady. "SO_2 Stack Emissions--1,000 ppm--A Reality." 1971 Annual Meeting of Pacific Northwest Air Pollution Control Association, International Section, Calgary, Alberta, November 1971.

57. Y. Barthel et al. "Treat Claus Tail Gas." Hydrocarbon Processing, 50 (5):89 (May 1971).

58. M. R. Bailleul et al. "Pollution and Sulfur Plants." National Convention NGPA, Denver, Col., March 1970.

59. G. L. Farrar. "Lacq Leads in Sulfur Recovery Operations." Oil and Gas Journal, October 19, 1970, p. 72.

60. G. Guyot and J. F. Martin. "The Sulfreen Process." Canadian NGPA, June 11, 1971.

61. F. M. Dautzenbert, et al. "Shell's Flue Gas Desulfurization Process." Chemical Engineering Progress, 67(8):86.

62. J. C. Davis. "SO_2 Absorbed from Tail Gas by Sodium Sulfite." Chemical Engineering, November 29, 1971, p. 43.

63. B. H. Potter. "The Wellman Lord SO_2 Recovery Process." Canadian NGPA, November 26,1971.

64. R. Dennis and R. H. Bernstein. " Engineering Study for Removal of Sulfur Oxides from Stack Gases." Prepared for API, August 1968.

65. F. T. Princiotta and N. Kaplan. Control of Sulfur Oxide Pollution from Power Plants. U. S. Environmental Protection Agency. Presented at Eascon 1972, Washington, D. C. (October 1972).

66. Evaluation of the Fluidized Bed Combustion Process. Vol. 1: Summary Report. Westinghouse Research Laboratories. EPA Contract No. CPA 70-9, Accession No. PB 211-494.

67. Reduction of Atmospheric Pollution (Vol. 1). British National Coal Board. EPA Contract No. CPA 70-97, Accession No. PB 212-960.

68. Evaluation of the Fluidized Bed Combustion Process. Vol. III: Appendices. Westinghouse Research Laboratories. EPA Contract No. CPA 70-9, Accession No. PB 213-152.

69. Development of Coal-Fired Fluidized Bed Boilers. U. S. Bureau of Mines R&D Report No. 36.

70. K. M. John. "Design of Fluidized Bed Combustors." Birmingham University Chemical Engr., 23, 1 (Spring 1972).

71. E. L. Carls. "Review of British Program on Fluidized-Bed Combustion," Report No. ANL/ES-CEN-1000 (August 1969).

72. R. H. Demmy. "Ignifluid Boilers for an Electric Utility." Proceedings of Second International Conference on Fluidized Bed Combustion, AP-109.

73. EPA Position Paper: "Pressurized Fluidized-Bed Combustion of Coal," (June 15, 1972).

74. G. P. Curran, et al. "Development of the CO_2 Acceptor Process Directed Towards Low-Sulfur Boiler Fuel." Annual Report on Contract No. EHSD 79-15 for period 1 Sept. 1970 - 1 November 1971.

75. A. V. Slack. "Air Pollution: The Control of SO_2 from Power Stacks." Chemical Engineer. (December 4, 1967).

76. G. M. Newcombe, M. A. Maxwell, and G. T. Rochelle. "Control of Sulfur Dioxide Emissions from Stack Gases—Discussion of Promising Soluble-Base Aqueous-Scrubbing Processes." U. S. Environmental Protection Agency. Presented at 17th Annual Meeting, Delaware Valley Section AIChE (March 1972).

77. J. Humphries, Jr., and W. A. McRae. "The Stone & Webster/Ionics Sulfur Dioxide Removal and Recovery Process." Presented at 2nd International Air Pollution Conference, Washington, D. C. (December 6-11, 1970).

78. "Flue-Gas Desulfurization Process To Be Developed." Oil and Gas Journal (January 12, 1970).

79. Coal News, No. 4135 (November 10, 1972).

80. Singmaster and Breyer. An Evaluation of the Atomics International Molten Carbonate Process. National Air Pollution Control Administration Contract No. CPA 70-76 (November 30, 1970).

81. P. M. Yavorsky, et al., Consolidation Coal Co., Library, Pa. Paper presented to Division of Water, Air and Waste Chemistry, American Chemical Society, Houston, Texas (February 1970).

82. J. B. Rosenbaum, et al. "The Citrate Process for Removing SO_2 and Recovering Sulfur from Waste Gases." U. S. Dept. of the Interior. Presented at AIME Environmental Quality Conference, Washington, D. C. (June 1971).

83. A. V. Slack. "An Introduction to Stack Gas Cleaning Technology." TVA. Presented at Technical Conference on Sulfur in Utility Fuels: The Growing Dilemma, sponsored by Electrical World, Chicago, Ill. (October 1972).

84. F. J. Ball, et al., Westvaco, North Charleston, S. C. Paper presented at 37th Midyear Meeting of American Petroleum Institute's Division of Refining, New York, N. Y. (May 1972).

85. W. R. Horlecher, et al. "Four SO_2 Removal Systems." Chemical Eng. Prog., 68 (August 1972).

86. Manuscripts of the reports of the VGB-Konferenz "Kraftwerk and Umwelt 1973".

87. VDI-Berichte Nr. 149, 1970 several articles on SO_2-removal processes.

4. CONTROL METHODS FOR INDUSTRIAL PROCESSES

Methods of treating industrial waste gases utilize processes for the recovery of sulfur either in elemental or in combined form. Although many of these methods overlap with combustion waste gas techniques, some gas treating processes are more often used for industrial application. These processes are discussed in this chapter, and flue gas cleaning processes are cross-referenced where appropriate. These processes also involve potential water pollution except for systems producing salable products which operate without purge streams as discussed in Section 3.4.

4.1 NONFERROUS PRIMARY SMELTERS

Information on various smelter SO_2 emission control systems is given in Table 4-1.

4.1.1 Sulfuric Acid Plants

The basic steps in the manufacture of sulfuric acid from smelter gases are shown schematically in Figure 4-1. Following cleaning of the smelter offgas to remove particulates, SO_3 is removed in an acid mist precipitator and the gas is dried with sulfuric acid. Prior to passing through a series of heat exchangers and catalytic converter stages to oxidize the SO_2 in the gases to SO_3, the dried gases are passed through an acid mist eliminator. Typically, three or four stages of converter catalyst are employed in this step. Finally, the SO_3 is absorbed by sulfuric acid to yield the product. The remaining gases are treated to remove droplets of acid and, in a single-absorption plant, are vented to the atmosphere or to systems similar to those used for SO_2 emission control of single-absorption sulfuric acid plants as discussed in Section 4.3. In a double-absorption plant, the gases from the absorption tower are passed again through a series of heat

Table 4-1. - SMELTER SO_2 EMISSION CONTROL SYSTEMS

Name/location	Comments
COPPER SMELTERS	
1. American Smelting and Refining Co. Tacoma, Washington	Currently treat 18 percent of converter gases in 1950 single-absorption H_2SO_4 plant. Installing DMA-liquid SO_2 system to treat remainder of converter gases 1973.
2. American Smelting and Refining Co. Hayden, Arizona	All converter gases treated in 1971 single-absorption sulfuric acid plant.
3. American Smelting and Refining Co. El Paso, Texas	All converter gases treated in 1973 double-absorption sulfuric acid plant.
4. Phelps Dodge Corp. Morenci, Arizona	Treat 100 percent of roaster gases in 1964 single-absorption H_2SO_4 plant.
5. Kennecott Copper Corp. Hayden, Arizona	All waste gases and 50 percent of converter gases treated in double-absorption sulfur acid plant converted from single-absorption in 1973.
6. Kennecott Copper Corp. Garfield, Utah	Converter gases treated in 5 single-absorption sulfuric acid plants installed in parallel.
7. Cities Service Co., Inc. Copperhill, Tennessee	All roaster, converter, and electric furnace gases treated in 4 single-absorption sulfuric acid plants or a 2-scrubber DMA-liquid SO_2 system installed in parallel.
8. Inspiration Consolidated Copper Co. Miami, Arizona	All electric furnace and converter gases treated in 1973 double-absorption sulfuric acid plant.
9. The Anaconda Co. Anaconda, Montana	About 60 percent of converter gases to be treated in a double-absorption sulfuric acid plant scheduled for activation in 1973.
10. Phelps Dodge Corporation Ajo, Arizona	Plan to install DMA single-absorption sulfuric acid plant emission control system to treat converter and reverberatory furnace gases on intermittent schedule.

Table 4-1. - SMELTER SO_2 EMISSION CONTROL SYSTEMS (Continued)

Name/location	Comments
11. Mitsubishi Metal Mining Co. Naoshima, Japan	
Smelter #1	All roaster and converter gases treated in either a single-absorption sulfuric acid plant or a chamber-type sulfuric acid plant installed in parallel. Tail gases from both acid plants treated in limestone-packed scrubbing tower.
Smelter #2	All roaster and converter gases treated in double-absorption sulfuric acid plant.
12. Onahoma Smelting and Refining Co. Onahoma, Japan	Roaster and converter gases treated in double-absorption sulfuric acid plant and caustic scrubbing system installed in series. Reverberatory furnace gases treated in single-absorbtion sulfuric acid plant and limestone-packed tower scrubbing system installed in series. Plan to apply lime scrubbing system to reverberatory furnace gases in conjunction with a new installation.
13. Nippon Mining Co., Ltd. Naoshima, Japan	All flash furnace gases treated in double-absorption sulfuric acid plant. All converter gases treated in single-absorption sulfuric acid plant and caustic scrubbing system installed in series.
14. Mitsui Mining and Smelting Co. Tamana, Japan	All flash furnace and converter gases treated in double-absorption sulfuric acid plant.
15. International Nickel Company Sudbury, Ontario, Canada	Flash furnace gases (80 percent SO_2) processed to liquid SO_2.
LEAD SMELTERS	
1. The Bunker Hill Co. Kellogg, Idaho	Strong gas stream (about 50 percent) of sintering machine gases treated in 1971 single-absorption sulfuric acid plant.
2. Missouri Lead Smelting Co. Boss, Missouri	Strong gas stream (about 30 percent) of sintering machine gases treated in single-absorption sulfuric acid plant.

Table 4-1. - SMELTER SO_2 EMISSION CONTROL SYSTEMS (Continued)

	Name/location	Comments
3.	St. Joe Minerals Corp. Herculaneum, Missouri	Strong gas stream of sintering machine gases treated in single-absorption sulfuric acid plant.
4.	Canadian Mining and Smelting Co. Trail, British Columbia, Canada	All smelter gases treated by ammonia scrubbing.
5.	Societe General de Hoboken Hoboken, Belgium	Roaster, sinter machine, and converter gases split to either chamber-type sulfuric acid plant or single-absorption sulfuric acid plant installed in parallel.
ZINC SMELTERS		
1.	American Smelting and Refining Co. Corpus Christi, Texas	All roaster gases to single-absorption sulfuric acid plant.
2.	American Smelting and Refining Co. Columbus, Ohio	All roaster gases to single-absorption sulfuric acid plant.
3.	National Zinc Co. Bartlesville, Oklahoma	All roaster gases to single-absorption sulfuric acid plant.
4.	The Bunker Hill Co. Kellogg, Idaho	All roaster gases to single-absorption sulfuric acid plant.
5.	St. Joe Minerals Corp. Monaca, Pennsylvania	All roaster gases to single-absorption sulfuric acid plant.
6.	The New Jersey Zinc Co. Palmerton, Pennsylvania	All roaster gases to single-absorption sulfuric acid plant.

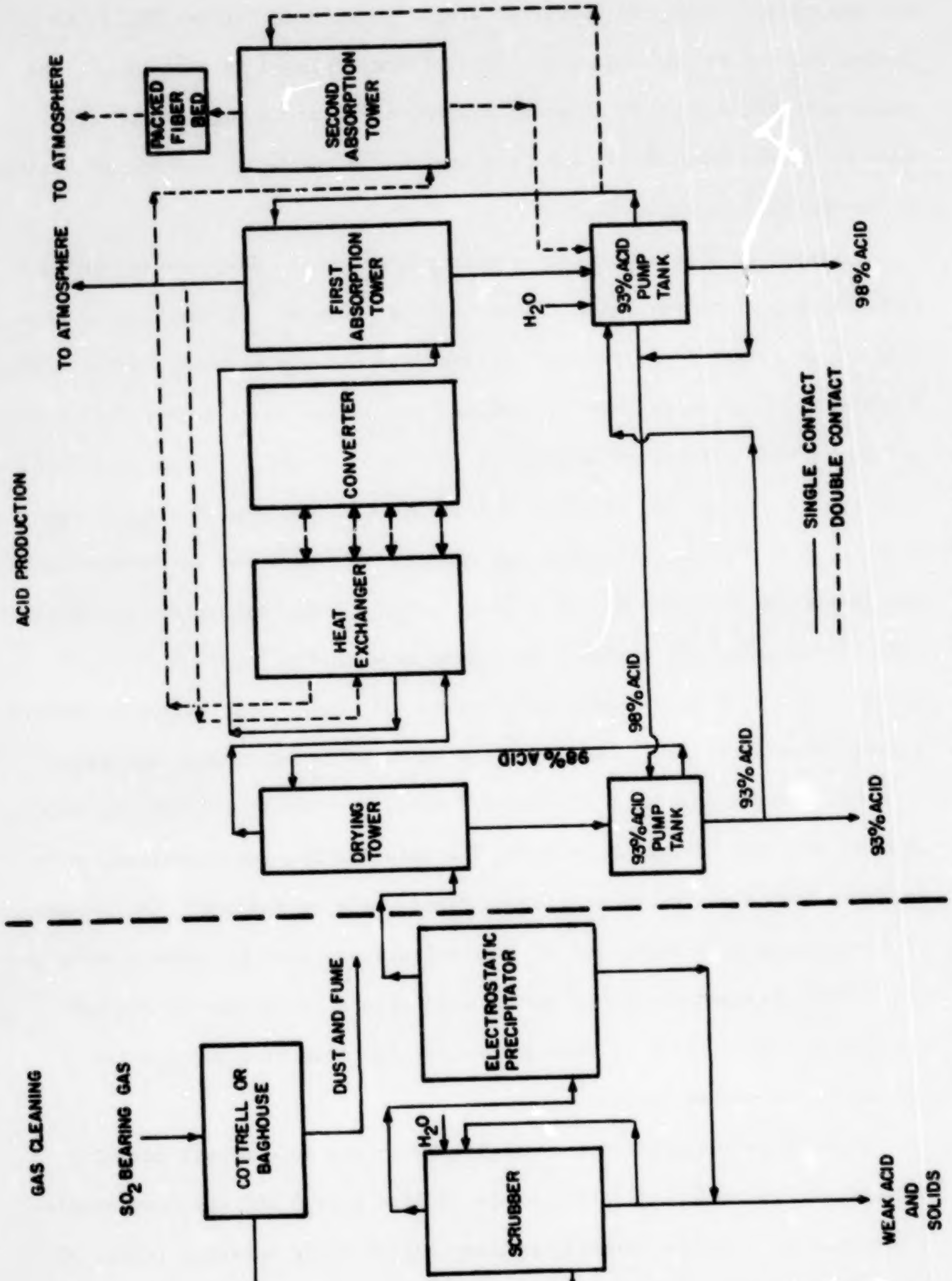

GAS CLEANING
ACID PRODUCTION
SO_2 BEARING GAS
COTTRELL OR BAGHOUSE
DUST AND FUME
H_2O
SCRUBBER
ELECTROSTATIC PRECIPITATOR
WEAK ACID AND SOLIDS
DRYING TOWER
93% ACID PUMP TANK
98% ACID
93% ACID
93% ACID
HEAT EXCHANGER
CONVERTER
98% ACID
FIRST ABSORPTION TOWER
TO ATMOSPHERE
H_2O
93% ACID PUMP TANK
98% ACID
SECOND ABSORPTION TOWER
PACKED FIBER BED
TO ATMOSPHERE
SINGLE CONTACT
DOUBLE CONTACT

Fig. 4-1. Sulfuric acid plants

exchangers and catalytic converter stages to oxidize further SO_2 to SO_3. Typically, one or two stages of catalyst are employed in this step. The gases are then routed to a second absorption tower through packed fiber beds to remove droplets of acid and are vented to the atmosphere or treated as mentioned in Section 4.3.

Single- or double-absorption acid plants can be designed to handle a wide variety of sulfur oxide concentrations; however, it may be more economical to apply other systems for treating weak gas streams. If more than 7 percent sulfur oxides are present, it is usually necessary to dilute with air to provide sufficient oxygen for conversion to SO_3. Gases containing less than 5 percent SO_2 frequently require extra cooling, and gases containing less than 3 percent SO_2 may require refrigeration to condense water and to prevent dilution of the product acid. Single-absorption sulfuric acid plants on offgas streams containing less than 3.5 percent SO_2 and double-absorption acid plants on offgases with an SO_2 concentration somewhat higher (about 5 percent) require fired heaters for continuous operation.[1-3]

For maximum operating efficiency, contact sulfuric acid plants should operate on a gas stream of uniform flow rate and SO_2 concentration, such as those from a fluid bed roaster or flash smelting furnace. Gas streams of fluctuating flow rates and SO_2 concentrations, such as those from copper converters, frequently do not permit acid plants to operate at maximum efficiency. Variations in feed gas volume are less of a problem than variations in concentration.[4]

With these qualifications, single-absorption acid plants normally achieve sulfur oxides emission levels of less than 3 000 ppm, and double-absorption acid plants normally achieve sulfur oxide emission levels of less than 500 ppm.

4.1.2 Elemental Sulfur Recovery Plants

None of the United States smelters currently operate elemental sulfur plants to recover sulfur from the sulfur dioxide contained in the smelter offgases. However, recently a domestic copper company announced the signing of contracts for the construction of a new copper smelter in the United States which will incorporate an elemental sulfur plant.[5] Outside the United States, there are reportedly three commercial-scale elemental sulfur plants operating: one in Finland, one in Canada, and one in Spain. The plant in Finland has been operating since 1963,[1] the plant in Canada has been operating for nearly two years at this point,[6] and the plant in Spain has been operating since 1955.[7] In addition, during the period from 1935 to 1943, elemental sulfur plants were operated in Canada and Sweden on smelter offgases.[8] As with sulfuric acid plants, elemental sulfur plants can be designed to operate on gas streams containing from a fraction of a percent of sulfur dioxide up to the highest concentrations feasible in smelter operations.[9] However, as the concentrations of SO_2 decrease, operating costs increase, since the consumption of reductant relative to the elemental sulfur produced increases.

The cost of the reducing agent is the major item influencing the economics of elemental sulfur plants.[9] As a result, minimizing the oxygen content in a gas stream to be reduced is of major importance since every volume of oxygen consumes as much reductant as a volume of sulfur dioxide. In addition, the heat released by the reduction of oxygen is an order of magnitude higher than that from the reduction of sulfur dioxide. Consequently, the control of reaction system temperatures by the removal of excess heat becomes a major consideration, frequently entailing increased expense as the oxygen content increases.

Depending on the extent to which heat integration is incorporated within the process, however, a certain minimum oxygen content will be required in the feed gas to achieve the high temperatures necessary for the reduction reactions to occur rapidly. The reduction of sulfur dioxide itself is only slightly exothermic, and as a result, in some cases it may be necessary to add dilution air to the offgases to insure that the reaction system will operate at the desired temperatures.

The reductant employed in elemental sulfur plants can be coke, pulverized coal, fuel oils, natural gases, or hydrogen.[9,10] In addition, sulfide ores themselves offer some potential. The reduction of sulfur dioxide with metal sulfides (such as copper sulfide ores) has received considerable experimental study. However, at this point no commercial-scale processes have been developed to utilize this concept.

Natural gas or fuel oil is frequently the choice of reductant where available, as they require a minimum of facilities for introduction and admixture into the gas stream to be reduced.

A recent elemental sulfur plant projected for operation on smelter offgases consists of three major sections, as shown schematically in Figure 4-2. In the first section, the offgases are cleaned and dried to remove particulates, water vapor, and acid mist. In the second section, reductant is mixed with the gas feed stream frequently in the presence of a catalyst to promote the reduction reactions. A portion of the sulfur dioxide contained in the gas stream reacts with the reductant to form hydrogen sulfide and elemental sulfur. The gases then pass into the third section, which is basically a Claus-type sulfur plant (see Section 3.3.3.2). Here in the presence of a catalyst, the hydrogen sulfide reacts with the

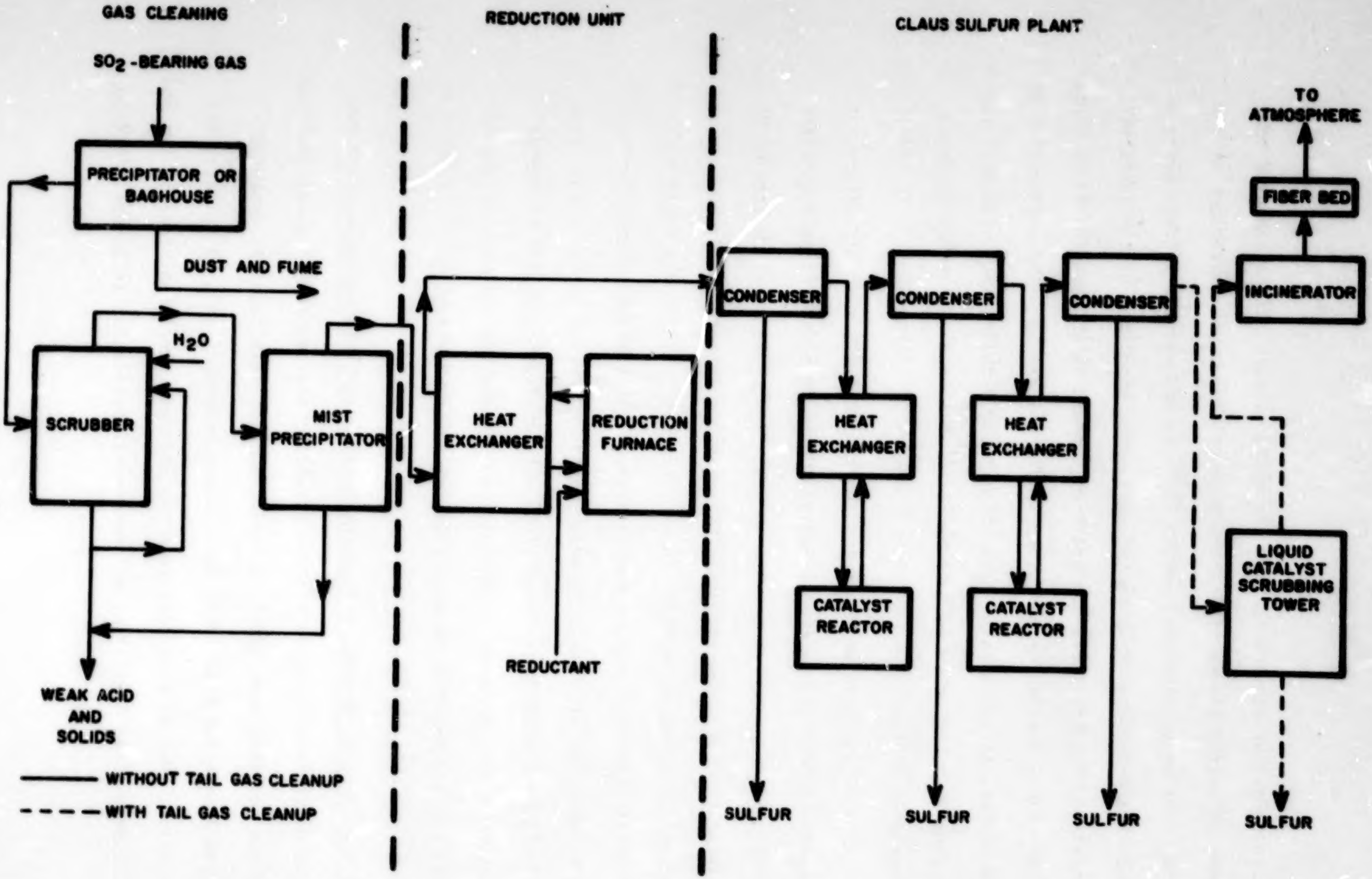

GAS CLEANING
REDUCTION UNIT
CLAUS SULFUR PLANT
SO2 -BEARING GAS
PRECIPITATOR OR BAGHOUSE
DUST AND FUME
H2O
SCRUBBER
MIST PRECIPITATOR
WEAK ACID AND SOLIDS
HEAT EXCHANGER
REDUCTION FURNACE
REDUCTANT
CONDENSER
HEAT EXCHANGER
CATALYST REACTOR
CONDENSER
HEAT EXCHANGER
CATALYST REACTOR
CONDENSER
INCINERATOR
FIBER BED
TO ATMOSPHERE
LIQUID CATALYST SCRUBBING TOWER
SULFUR
SULFUR
SULFUR
SULFUR
WITHOUT TAIL GAS CLEANUP
WITH TAIL GAS CLEANUP

Figure 4-2. Elemental sulfur plant.

remaining sulfur dioxide to form elemental sulfur. It is expected that elemental sulfur plants will achieve about 90-percent conversion of the sulfur dioxide to elemental sulfur.[6,10] In addition, a process using a liquid Claus-type catalyst has recently been developed by the Institute Francais du Petrole (IFP) and has been commercially demonstrated on Claus sulfur plants within the petroleum refining industry. The application of this process to the exhaust gases from these metallurgical elemental sulfur plants is projected to increase the conversion efficiency to about 98 percent.[11,12]

As with sulfuric acid plants, for maximum operating efficiency, elemental sulfur plants should operate on a gas stream of uniform flow rate and SO_2 concentration, such as that from a fluid bed roaster or flash smelting furnace. Gas streams of fluctuating flow rates and SO_2 concentrations, such as those from copper converters, frequently would not permit an elemental sulfur plant to operate at maximum efficiency. In these cases, as with sulfuric acid plants, elemental sulfur plants must be designed for the worst conditions with adequate controls to handle changes in concentration. Fluctuations in feed gas volume are less of a problem and could be tolerated within reasonable limits.

4.1.3 Scrubbing systems

4.1.3.1 Organic Scrubbing (Dimethylaniline and Related Compounds)--The early development work on organic scrubbing systems for offgases from nonferrous smelters was done in Europe. Much of this work was centered around dimethylaniline (DMA) and similar compounds such as xylidine and toluidine. Out of this work came two separate processes--namely, DMA and Sulphidine--that found limited commercial application in Europe. Although one DMA unit has been installed in Norway and another has been installed in Spain, most of its application has been in the United States.

In 1947, the American Smelting and Refining Company (ASARCO) installed the first domestic DMA unit at their Selby, California, lead smelter to remove SO_2 from the offgases of a Dwight-Lloyd sintering machine. In 1949, a DMA system was installed at Copperhill, Tennessee. These DMA operations generally scrub gases that contain at least 5 to 6 percent SO_2.[13] Absorber efficiencies have been reported to be about 500 ppm at Selby and in the range of 3 000 to 3 500 ppm at Copperhill. Although the ASARCO Selby smelter has been shut down, the Tennessee DMA system is still in operation.

New units are currently being planned at the smelters at Ajo, Arizona,[14] and Tacoma, Washington.[15] Although the Tacoma unit will scrub strong gases, the unit at Ajo will, at times, process gases as dilute as 0.5 percent SO_2.

The absorption section of the DMA process utilizes a high pressure drop scrubber which is divided into three sections (see Figure 4-3). The SO_2 absorption takes place in one of the sections, and the other two perform functions that are related to recovery of lost sorbent. As part of the process of regenerating the sorbent, a waste product of about 0.02 kg of sodium sulfate is produced per kg of SO_2. These wastes have water pollution potential. Since this product rate is a strong function of the rate of oxidation in the scrubbing circuit (which is higher at lower inlet concentrations), the quantity of waste sulfate is somewhat higher when scrubbing weak streams. Due to the effectiveness of the absorbent recovery scheme, only very small quantities of DMA are lost. The product of the DMA scrubbing process is a very pure liquid sulfur dioxide.

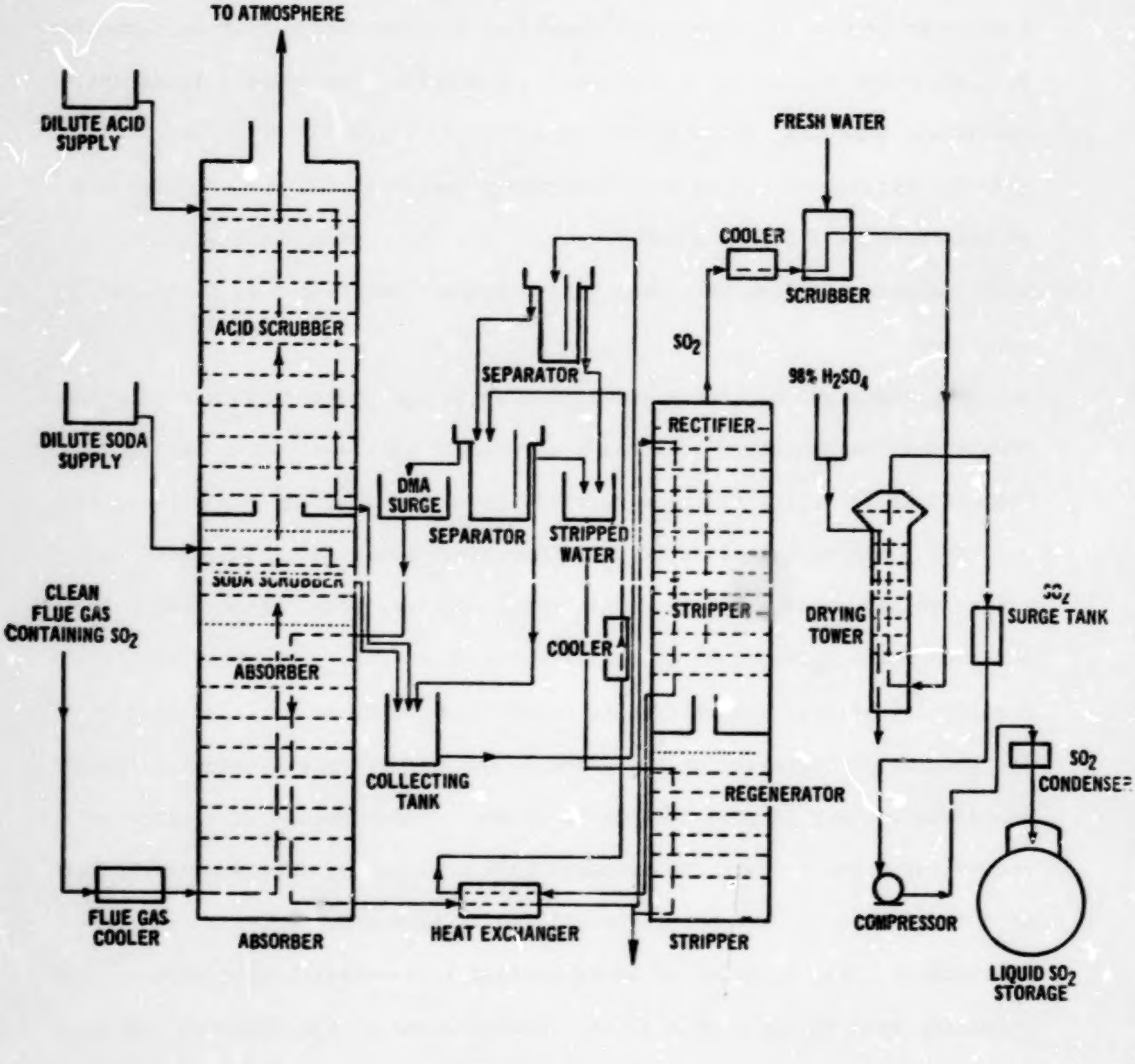

TO ATMOSPHERE
DILUTE ACID SUPPLY
ACID SCRUBBER
DILUTE SODA SUPPLY
SODA SCRUBBER
CLEAN FLUE GAS CONTAINING SO2
ABSORBER
FLUE GAS COOLER
ABSORBER
SEPARATOR
DMA SURGE
SEPARATOR
STRIPPED WATER
COOLER
COLLECTING TANK
HEAT EXCHANGER
FRESH WATER
COOLER
SCRUBBER
SO2
98% H2SO4
RECTIFIER
STRIPPER
REGENERATOR
STRIPPER
DRYING TOWER
SO2 SURGE TANK
SO2 CONDENSER
COMPRESSOR
LIQUID SO2 STORAGE

Fig. 4-3. DMA process.

From a process standpoint, the ASARCO DMA systems are quite similar to the European-developed Sulphidine process[16] which utilizes an aqueous xylidine scrubbing medium and is primarily applicable to lower SO_2 concentration inlet streams (i.e., less than 3 percent SO_2) than is DMA. The Sulphidine process has been used experimentally on gases that varied in SO_2 concentration from 0.5 to 8.0 percent and has yielded offgas streams with concentrations as low as 500 to 1 000 ppm.

4.1.3.2 Lime/Limestone Scrubbing Systems--These systems, although primarily used for flue gas cleaning, might also be used to remove SO_2 from weak smelter offgases. Process details are similar to those discussed in Section 3.4.

4.1.3.3 Sodium Sulfite/Bisulfite Scrubbing Systems--Most of the development work on a sodium sulfite-bisulfite scrubbing system in this country has been conducted by Wellman Power Gas (formerly Wellman-Lord). Although primary emphasis has been on flue gas applications, pilot units have been tested on converters and smelter reverberatory furnaces. A more detailed discussion is in Section 3.4.

4.1.3.4 Ammonia Scrubbing Systems--In the early 1930's, the first ammonia scrubber was installed at the Cominco (Canadian Mining and Smelting Company of Canada) smelter in Trail, British Columbia, for the purpose of recovering sulfur dioxide. This unit, installed on a lead sintering machine with an average offgas concentration of approximately 0.75 percent SO_2,[17] was followed by similar scrubbing systems on all the offgases that contain significant concentrations of SO_2. About 90 percent of the input sulfur to the smelter is recovered in the form of usable products.[18] Typically, exit gases from ammonia scrubbers have SO_2 concentrations of less than 1 000 ppm.

At least three variants of the ammonia scrubbing system have been commercially applied. In all three, SO_2 reacts with aqueous ammonia to give ammonium sulfite and bisulfite. The differences occur in the manner in which the liquid effluent from the scrubber is treated.

The basic Cominco process (see Figure 4-4) utilizes a chemical stripping step to produce ammonium sulfate and sulfur dioxide. This process is carried out by acidification of the scrubber liquor with sulfuric acid. Consequently, large quantities of byproduct ammonium sulfate result. In locations where ammonia is expensive or when the production of ammonium sulfate would generate a solid waste disposal problem, chemical stripping may not be as attractive.[19]

The other two major variants of this process utilize thermal decomposition of the ammonium salts. The first heat regenerative process, developed on a pilot scale by ASARCO but first put to commercial use at the Cominco smelter in Trail, British Columbia, became known as the "exorption process." One of the major problems with this system is the formation of ammonium sulfate,[20] either by reaction with sulfur trioxide in the gas or through oxidation of sulfite in the liquid. Ammonium sulfate must be removed from the liquor either by using a purge stream or by incorporation of a crystallization step. Compared to the chemical stripping regeneration, the exorption process produces less sulfate to be discharged and also minimizes the amount of ammonia required.

The third type of regeneration which has been practiced commercially on sources other than smelters was developed by Chemiebau in Europe.[21] The effluent liquid containing ammonium sulfite, bisulfite, and sulfate is sprayed into a combustion chamber and thermally decomposed to give SO_2,

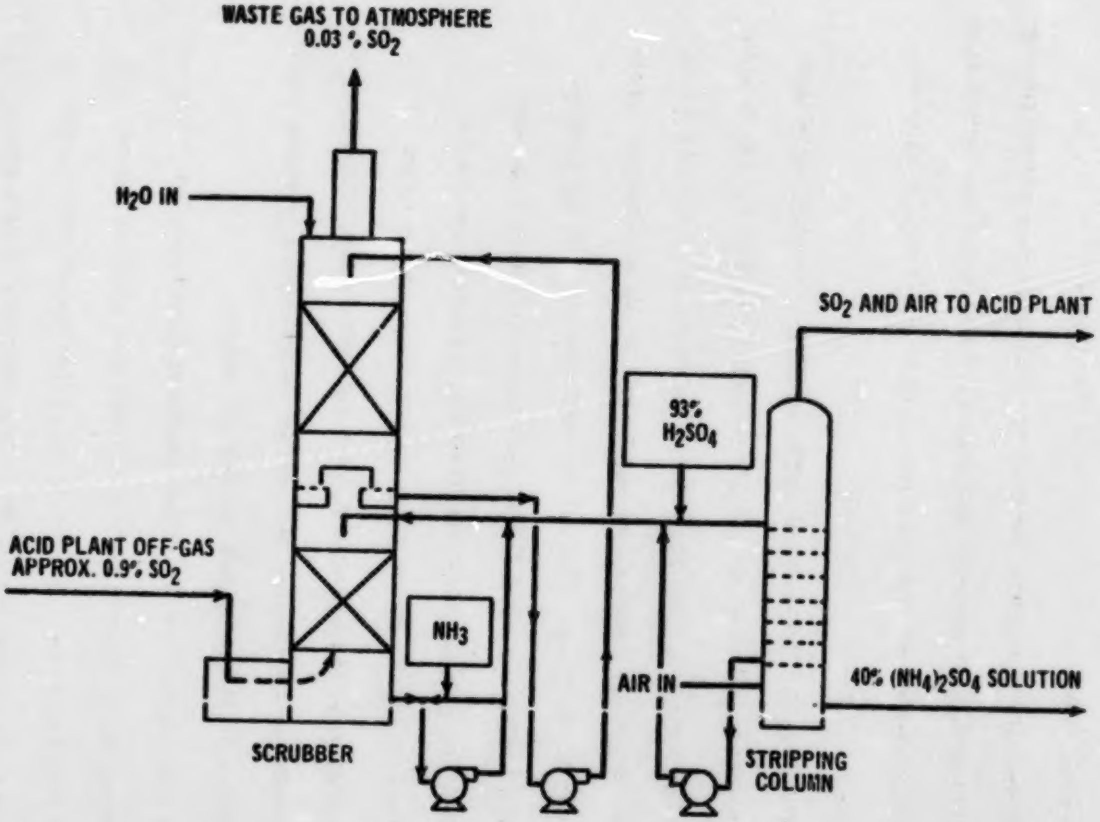

WASTE GAS TO ATMOSPHERE
0.03 % SO_2
H_2O IN
SO_2 AND AIR TO ACID PLANT
93% H_2SO_4
ACID PLANT OFF-GAS
APPROX. 0.9% SO_2
NH_3
AIR IN
40% $(NH_4)_2SO_4$ SOLUTION
SCRUBBER
STRIPPING
COLUMN

Fig. 4-4. Type of SO_2 recovery process.

H_2O, and N_2. The combustion products can be further processed in an acid plant (Section 4.1.1) or a Claus plant (Section 3.4). Thermal regeneration eliminates any sulfate disposal problems; however, it consumes as much ammonia as does chemical stripping.

4.1.4 Emission Control Costs

Air pollution control costs are subject to a wide number of variables as discussed in Section 3.4. Smelter emission control costs are subject to additional variables related to the type of smelter and the emission control schemes involved.

1973 EPA cost estimates for sulfur oxide emission control at a new smelter producing 75 Mkg per year of copper ranged from \$12 to \$32.5 million capital costs and from 5.1 to 12.5 cents annualized costs per kg of copper produced.[22] The lower estimates represent 60 to 80 percent efficient total smelter SO_2 emission control by the application of single-absorption sulfuric plants to selected high-concentration gas streams. The higher estimates represent total smelter SO_2 emission control efficiencies--on the order of 99 percent--by application of high-efficiency systems such as double-absorption sulfuric acid, elemental sulfur, and/or scrubbing systems to all offgases and which include provision for disposal of all recovered sulfur as waste.

Similar cost estimates for new zinc smelters producing 90.7 Mkg of zinc per year ranged from \$5 million to \$23 million capital costs with annualized costs ranging from 1.5 to 6.8 cents per kg of zinc produced. Similar capital cost estimates for a 90.7-Mkg-per-year lead smelter ranged from \$5 to \$15 million with annualized costs ranging between 1.5 and 4.4 cents per kg of lead produced. Costs for retrofitting existing smelters could be as much as double that for new smelters.[1]

In some cases, it may be possible to defray emission control costs by sale or use of products such as sulfur, sulfur dioxide, sulfuric acid, ammonium sulfate, or gypsum. The feasibility of these alternatives varies from smelter to smelter.

4.2 PETROLEUM REFINERIES

With some exceptions, refinery SO_2 emissions originate from the burning of sulfurous fuels or wastes. Control techniques which are applied for desulfurization of liquid and gaseous refinery fuels or wastes are discussed in Sections 3.3.2 and 3.3.3. Although flue gas desulfurization systems (see Section 3.4) might possibly be applied in lieu of fuel desulfurization, there are no such full-scale applications at U.S. refineries. Other refinery sources which are not amenable to fuel desulfurization techniques but which might possibly be controlled by flue gas desulfurization techniques are catalytic cracking, catalyst regeneration systems, and fluid bed cokers.

4.3 SULFURIC ACID PLANTS

Among the sulfur oxide emission control processes now being used for sulfuric acid plants are multiple-stage contact and absorption, sodium sulfite scrubbing, ammonia solution scrubbing, alkaline scrubbing, and molecular sieve separation. Scrubbing systems are discussed in Sections 3.4 and 3.5.1.3

4.3.1 Multistage Contact and Absorption

The efficiency of conversion of SO_2 to sulfuric acid in contact-type sulfuric acid plants is increased by increases in contact and absorption. Increases in the number of stages of catalyst effects some measure of emission reduction, and increases in the number of absorption stages effects further emission reduction as described in Sections 2.2.3.2 and 2.2.3.3. In summary, inefficient single-absorption sulfuric acid plants emit as much as 50 kg of SO_2 per 1 000 kg of acid produced (several thousand ppm) as compared with the most efficient dual-absorption plants which, under some conditions, emit less than 0.5 g of SO_2 per kg of acid produced (about 60 ppm).

Multistage contact and absorption techniques are commonly applied in the design of new sulfuric acid plants rather than for upgrading the efficiency of existing plants because other SO_2 emission control techniques are usually applied more economically to existing single-absorption plants. An exception to this is cited in Table 4-1.

4.3.2 Sodium Sulfite Scrubbing

The Wellman Power Gas process (Section 3.4) has been operating satisfactorily since early 1971 on a sulfuric acid plant operated by Olin Corporation in Paulsboro, New Jersey. Sulfur dioxide emissions from this plant have been reduced from 5 000-6 000 ppm to 200-300 ppm, or below approximately 1.45 kg per 1 000 kg acid. Several other acid plants are scheduled to install this process in the near future.

Sodium sulfite scrubbing systems on sulfuric acid plants have also been used to produce sodium sulfite for use by ammunition plants. This process is being installed at the Newport, Indiana, Army Ammunition Plant for controlling a 0.94-Mkg/day spend-acid plant. The scrubber is designed so that outlet sulfur dioxide emissions will be less than 100 ppm.

A Japanese sodium sulfite scrubbing system installed on a 0.91-Mkg/day sulfur-burning dual-absorption plant in the Chiba Prefecture reduces SO_2 emissions from about 600 ppm to 17 ppm SO_2.[23] This Mitsui-Monsanto plant added the Ebara-designed (Showa-Denko) scrubber to meet Chiba Prefecture H_2SO_4 plant regulations which prohibit emissions in excess of 50 ppm SO_2. The resultant 20-percent sodium sulfite solution is sold to the pulp industry and to other consumers.

4.3.3 Ammonia Scrubbing

Several ammonia scrubbing systems have been applied to sulfuric acid plants in the United States. Allied Chemical's sulfuric acid plant at Newell, Pennsylvania, uses an ammonia scrubbing system to control SO_2 emissions to below 100 ppm. A high-efficiency mist eliminator is used to control particulate emissions to less than 20 percent capacity. The spent scrubbing liquor is reacted with weak acid releasing SO_2 to the process. The resultant solution is incinerated in the purite roaster to recover the remaining sulfur content or used to eliminate windblown dust from the iron oxide cinder pile.

4.3.4 Alkaline Scrubbing

At times, tail gases from single- or double-absorption sulfuric acid plants are scrubbed with limestone, lime, caustic, or sodium sulfite. Examples of applications are given in Figure 3-32 and Table 4-1. Outlet SO_2 concentrations as low as 20 ppm have been reported from the Onahoma Smelting and Refining Company system described in Table 4-1.

The problems of water pollution and waste disposal associated with these systems is similar to those mentioned in Section 3.4. A sulfuric acid plant at the Koyasu Mill of Nippon Kokan, Japan, is equipped with a lime scrubbing system which is of closed-loop design. This system has operated according to design since 1965, producing a usable gypsum product without discharge of wastewater.

4.3.5 Molecular Sieve Separation

In the molecular sieve separation process, the absorber overhead stream first passes through a mist eliminator and then into an absorbent bed. The SO_2, as well as traces of acid mist, particulates, SO_3, and H_2SO_4 vapor, are completely removed from the tail gas before venting to the atmosphere. Just before the bed becomes completely saturated with SO_2, the feed gas is switched to an alternate bed, and the saturated bed is regenerated with a purge of hot, dry air.

The effluent purge stream, rich in SO_2, is fed back into the acid plant for conversion to sulfuric acid. The entire adsorption/regeneration cycle operates continuously on an automatically timed basis.

A commercial version of this process was developed for sulfuric acid plants by Union Carbide and is licensed to Monsanto/Enviro-Chem. The first commercial installation is scheduled for startup by late 1972 at Coulton Chemical Company's new sludge acid plant near Toledo, Ohio. The maximum guaranteed emission level for this installation is 100 ppm of SO_2 and an absorbent life of at least one year. The expected emission is only 10 to 20 ppm SO_2, and the absorbent is expected to last at least two years.

4.4 IRON AND STEEL PLANTS

4.4.1 Coke Oven Gas Desulfurization

The prime technology applied in the United States for coke oven gas desulfurization is the vacuum carbonate process. The Stretford, Takahox, and Fumaks processes are also applied to coke oven gases. No control methods are in use in the BRD.

The vacuum carbonate process includes the process for stripping H_2S from the gas and any associated recovery systems. Information on various

Table 4-2. - IRON AND STEEL PLANT SULFUR REMOVAL SYSTEMS - VACUUM CARBONATE PROCESS

Company name and location	Type gas cleaned	Plant size $10^6 m^3$/day	Number units	Status	Sulfur recovery
Bethlehem Steel Corp. Bethlehem, Pa.	COG[1]	0.57	1	Idle	No
Bethlehem Steel Corp. Johnstown, Pa.	COG	0.57	1	Shut down	No
Bethlehem Steel Corp. Lackawanna, N.Y.	COG	0.57	2	Operating	Yes, contact acid plant[2]
Bethlehem Steel Corp. Sparrows Point, Md.	COG	1.14	1	Operating	Yes, contact acid plant[2]
		0.57	3	Operating	Yes, contact acid plant[2]
Denner Hanna Coke Buffalo, N.Y.	COG	0.86	1	Operating	No
Koppers Company, Inc. Kearny, N.J.	COG	1.36	1	Shut down	No
Pittsburgh Coke & Chemical (now Shenango, Inc.) Neville Island, Pa.	COG	1.14	Unknown	Shut down	No
Republic Steel Corp. Cleveland, Ohio	COG	Unknown	1	Shut down	No
Wheeling-Pittsburgh Steel Corp. East Steubenville, W.Va.	COG	0.43	1	Unknown	No
Bethlehem Steel Corp. Burns Harbor, Ind.	COG	3.42	Unknown	Operating	Yes, Claus plant
National Steel Corp. Weirton, W.Va.	COG	1.72	Unknown	Scheduled	Yes, Claus plant
Dominion Foundry & Steel Co., Ltd. Hamilton, Ontario	COG	0.79	1	Operating	___

[1] COG refers to coke oven gas.

[2] Plans are currently underway to replace this contact acid plant with a Claus unit.

North American applications of this process are given in Table 4-1. In the vacuum carbonate process, the hydrogen sulfide is absorbed in a 3 to 3.5 percent solution of sodium carbonate which is subsequently steam stripped under vacuum. The efficiency of H_2S removal for this process is about 90 percent for older plants and 93 percent for plants of more recent vintage.[24]

The H_2S from the stripping process is wasted or converted to sulfuric acid or sulfur as shown in Table 4-2. The steam jet condensates from this process have water pollution potential.

The Stretford process produces elemental sulfur directly from coke oven gas containing H_2S by chemical reactions involving anthraquinone disulphonic acid, complex ammonium-sodium-vanadium compounds, and buffering compounds. Removal efficiencies in excess of 99 percent have been reported.[25] The process is reportedly applied to several European plants and to the plant cited in Table 4-2. The Takahax and Fumaks processes applied in Japan also produce elemental sulfur directly from coke oven gases containing H_2S. The liquid wastes from these processes have water pollution potential.

4.4.2 Sintering Plant Gas Treatment

Because of the low SO_2 concentrations and large gas volumes involved, SO_2 emission control systems are not commonly applied to iron and steel plant sintering operations. A pilot plant designed to treat 12.2 m^3/s of gas from a Japanese iron-ore sintering plant has been in operation since 1969. This system involves sea water scrubbing to remove particulate matter followed by SO_2 absorption in a dilute ammonia solution. The ammonium sulfite is subsequently oxidized to ammonium sulfate. The system reportedly reduces inlet concentrations varying between 600 and 1 000 ppm to outlet concentrations varying from 50 to 80 ppm. A 61.3-m^3/s system such as this is reportedly being applied to the iron-ore sintering plant at the Keihin Works of Nippon Kokan in Japan.[26]

EPA personnel have located and plan to test a 21.2-m^3/s limestone scrubbing system installed on an iron-ore sintering and pelletizing plant at the Yahagi Iron Company, Nagoya, Japan.[27]

It is possible that one or more of the processes for flue gas desulfurization might be applied to iron-ore sintering plants (see Section 3.4).

4.4.3 Emission Control Costs

Dunlap, et al., have estimated costs for treating 1.69×10^6 Nm^3 of coke oven gas per day by vacuum carbonate-Claus process emission control combinations and by the Stretford process.[24] Capital cost estimates ranged from \$2.3 million to \$3.3 million with estimated annualized costs ranging from 0.1 to 0.13 cents per Nm^3 of gas processed or from 0.44 to 0.61 cents per 10^3 kg of coke produced.

4.5 PULP AND PAPER MILLS

Control methods differ somewhat for the various pulp and paper processes, the sulfate process, the sulfite process, and the neutral sulfite semichemical process. The sulfite process is used exclusively in the BRD. Paper mill steam and power boilers must also be considered.

4.5.1 Sulfate (Kraft) Process Emission Control

Control devices are not used specifically for SO_2 control at sulfate mills. Reduction of SO_2 emissions is incidental to the reduction of odors and particulates. Sufficient secondary air, turbulence in the secondary zone, and liquor spray pattern can substantially reduce recovery furnace emissions of odorous sulfur compounds and SO_2.[28] Tables 4-3 through 4-5 show the effects of operating variables on SO_2 emissions. The scrubbing action which takes place in direct-contact evaporators reduces SO_2 emissions. Careful process control using emission monitoring techniques also allows the recovery furnace to operate at reduced odorous and SO_2 emission levels.

Scrubbers are normally used on lime kilns to control particulates and some odorous emissions. Lime kiln scrubbers also effect some reduction of SO_2 emissions.

4.5.2 Sulfite Process Emission Control

The SO_2 emissions from combustion are recovered by absorption in the scrubber and the three absorption towers. Systems for absorption of relatively strong SO_2 gases in the appropriate base are fairly well established; however, SO_2 emissions from these systems can be significant unless processes are properly controlled and maintained. Proper flow rates, temperatures, and concentrations of the SO_2 gas and absorption solution minimize atmospheric emissions and process losses. Gases from the digester and the blow tank can be controlled by passing them through condensers and absorption towers or caustic scrubbers. One mill reported a net savings of over $250,000 a year from recovery of sulfur by installation of a condenser and absorber to control SO_2 emissions from blow tanks.[30]

4.5.3 Neutral Sulfite Semichemical Process Emission Control

As with the other sulfite pulping processes, emissions are greatly reduced by efficient absorption and recovery of the SO_2.

4.5.4 Steam and Power Boiler Emission Control

One unique control technique for SO_2 emissions from boilers at a kraft mill has been proposed.[31] The method would involve scrubbing power

Table 4-3. - EFFECTS OF FUR[illegible] SECONDARY AIR ON SO_2 AND OTHER SULFUR COM[illegible]MISSIONS[29]

Secondary air, percent	Excess O_2, percent	[illegible]	H_2S, ppm
28.5	1.4	96.7	24.6
30.0	1.2	53.0	12.6
36.5	2.6	0.1	0.007
41.0	3.4	0.2	0.012

Table 4-4. - EFFECTS OF TURBULENCE ON FURNACE GASEOUS EMISSIONS[29]

Velocity at secondary airport outlet, m/s	SO_2, ppm	H_2S, ppm
54	0.2	0.012
20	47.1	84.5

Table 4-5. - EFFECTS OF LIQUOR SPRAY PATTERN ON FURNACE GASEOUS EMISSIONS[29]

Type spray	SO_2, ppm	H_2S, ppm
Coarse	0.08	0.0
Fine	9.8	0.37

boiler flue gases with black liquor from the kraft process. The SO_2 absorbed in the liquor would add sulfur to the cooking liquor and thereby reduce makeup requirements. In mills where high-sulfur fuels are burned, it might be necessary to limit sulfur recovery by such a system to avoid exceeding sulfur makeup requirements. A sodium carbonate scrubbing system has also been proposed.[32] Control systems for combustion processes (Section 3.4) might also be applied to these boilers.

4.6 WASTE DISPOSAL

4.6.1 Coal Refuse

Pretreatment of waste prior to deposition--i.e., utilization of improved coal preparation techniques to reduce the carbonaceous and combustible organic material--can be effective in preventing fires. During deposition of the refuse, the waste pile can be constructed to inhibit ignition. The pile should be built up in layers, and each layer should be compacted and then covered with a noncombustible material of low permeability such as clay. Clay should also be used to seal the edges of the bank. A layer of loose material capable of supporting vegetation should be added, and fencing and posting can minimize the chance of ignition by trespassers.

Early efforts to extinguish coal refuse fires began in England during World War II and involved saturation sprinkling of the burning refuse with water. This technique proved effective while there was a continuous flow of water, but the fires usually rekindled after sprinkling was terminated.[33] Several other generally ineffective techniques have been tried. Blanketing refuse banks with clay or dirt to restrict the flow of air to the burning pile is usually unsatisfactory since the seal eventually becomes ineffective if left untended. Saturation sprinkling with drainage into 3.05 m boreholes and injecting water directly into the piles have not been successful methods for extinguishing fires.

In 1968, the U.S. Bureau of Mines completed a demonstration project considered a step toward developing a successful and low-cost procedure for quenching and removing burning coal refuse.[33] Various combinations of high-pressure water cannons and earth-moving equipment were used to quench, dislodge, and remove the refuse to an adjacent area. The material was then compacted and covered with available noncombustible material. Complete extinguishment was accomplished at a cost of about $0.58 per cubic meter. In addition, the Bureau of Mines has successfully demonstrated two other techniques. In the "rice paddy" method, the entire surface of the coal refuse bank is leveled and divided into a number of shallow ponds by creating low berms of refuse material. The ponds are flooded, and the percolation of the water into the bank is enhanced by disturbing the pond bottoms with a drag line. This method minimizes the amount of material that must be moved and is particularly suited to banks surrounded by urban development. In another method recently used to extinguish the National Refuse Bank in Scranton, Pennsylvania, a grid network of perforated pipes is installed in shallow boreholds. Water is pumped through the pipes to quench a layer of the bank. This layer is subsequently removed, redeposited on a nearby site, and graded to conform with the local topography.

An extensive program to evaluate various coal refuse fire extinguishing techniques has recently been completed under the co-sponsorship of the U.S. Environmental Protection Agency and the States of Kentucky, Pennsylvania, and West Virginia.[34] A total of fifteen demonstration projects involved variations and combinations of three basic control techniques. These were:

1. Sealing or capping--to prevent oxygen from reaching the hot zones of the bank. Materials used as sealants included polyurethane and plastic foams, fine limestone, waste dust from cement plants, and an asphaltic emulsion.
2. Grouting--the injection of a slurry into the hot zone of the pile. Slurries consisted of various mixtures composed primarily of water, limestone, vermiculite, and sodium bicarbonate.
3. Mechanical-hydraulic methods--water used as the extinguishing medium. Quenched material is subsequently repiled and compacted.

In general, mechanical-hydraulic methods were the most successful from the standpoint of positive extinguishment and demonstrated moderate unit costs of $0.86 to $1.49 per cubic meter. Some sealing methods yielded low unit costs of $0.26 to $1.36 per cubic meter, but they were not successful in completely extinguishing the fires; the one sealing project that was successful had a rather high unit cost of $4.39 per cubic meter. Three of the four grouting projects were unable to extinguish the fires completely and gave high unit costs of $1.96 to $8.51 per cubic meter. The fourth grouting project was successful and yielded an acceptable unit cost of $1.63 per cubic meter.

Of these fifteen demonstration projects, seven were judged to have produced good results both economically and from the standpoint of the technology involved in extinguishing coal refuse fires. These seven projects are summarized in Table 4-6.

Table 4-6. - SUCCESSFUL DEMONSTRATION METHODS FOR EXTINGUISHING CULM-BANK FIRES[34]

Project number	Location	Method demonstrated	Material processed or extinguished (cu meters)	Cost per meter^3
1. 67A-4112-D	Rossini Coal Co., Fails Slops Shamokin, Pa.	Grout - Using lime/limestone slurry; pile covered with limestone refuse.	24,500	$1.64
2. 67A-411-D	Ruch and Pittsburgh Bank, Iselin, Pa.	Seal - Using polyurethane foam after shaping pile and quenching hot spots with water.	38,200	4.39
3. 66A-4101-D	Huber Bank, Ashley, Pa.	Quenching - Bulldozers and drag lines.	258,000	1.49
4. 66A-4106-D	Westmoreland Coal Co. Mine, White Station, Pa.	Water Sprinkling - Dig out with dozer; repile in compact layers.	73,000	0.86
5. 66A-4108-D	Baker Bank, Scranton, Pa.	Explosive Breakup - Of portions of bank followed by water quenching and dozer removal to disposal area.	12,600	2.86
6. 67A-4109-D	Lackawanna County, Pa.	Water Monitors - Quenching and removal using drag lines, carryalls, and dozers.	450,000	0.99
7. 68A-4113-D	Huber Bank, Ashley, Pa.	I. Water Monitors and Lagoons - Drag lines, carryalls, and dozers.	200,000	0.93
		II. Water Monitors and Lagoons - Same as Method I but spray hot spots with monitors; deposition of material in dispenser area in alternate layers and compacted.	145,000	1.36

4.6.2 Other Refuse Incineration

At present, control of SO_2 emissions from incinerators is not being practiced. However, some of the flue gas desulfurization processes discussed in Section 3.4 might be used to desulfurize incinerator stack gases should SO_2 emission controls become desirable.

4.6.3 Sewage Sludge

Existing control techniques are motivated primarily by the need to avoid corrosion and involve removal of H_2S from the sewer gas prior to storage or use. Scrubbing with water or sewage effluent, augmented by the addition of chlorine to the gas, can reduce H_2S concentrations from over 4.56 g/m^3 to 1.14 g/m^3 or less.[35] Further treatment of the scrubbing solution may then be required before disposal. Another technique involves H_2S absorption by "iron sponge," a mixture of ferric oxide and hardwood shavings.[35,36] The iron sponge is then regenerated by exposure to air, releasing sulfur as SO_2. This is generally emitted to the atmosphere, but it could be absorbed by alkali solutions or by one or more of the flue gas desulfurization techniques discussed in Section 3.4. Other scrubbing techniques, such as those used in desulfurizing refinery process gases as discussed in Section 2.2.2.10, might also be effective in removing H_2S from sewer gases.

Incineration is one of the most effective techniques for sewage sludge disposal although other methods, such as land filling and use as fertilizer are sometimes acceptable. Since incineration has an inherent potential for air pollution, sludge incinerators (like other incinerators) must be properly designed and operated to meet existing air quality standards. Sludge incinerator stack gases include particulates, nitrogen oxides, sulfur dioxide, and varying quantities of metals and metal oxides depending on local sludge composition. Sulfur dioxide, produced upon partial oxidation of some of the sulfur compounds in sludge, is not usually a problem. Although analyses have shown the average sulfur content of municipal sludges to be about 1 percent,[37] much of this sulfur is in the form of sulfates or other stable compounds and is not converted to SO_2 during incineration. Emission factors measured at several incinerators were found to be less than 0.75 kg SO_2/1 000 kg of sludge burned, while average SO_2 concentrations were within 13 ppm. In general, control of sulfur oxide emissions from sewage sludge incinerators is not now being practiced; however, a wet oxidation method for sludge treatment, used on a large scale in Chicago, does develop some SO_2 control as an incidental benefit by oxidizing sulfur compounds to sulfates prior to incineration. In this process, a 3-percent aqueous suspension of ground sludge from primary settlers is pumped into a heated system (about 547 K) where the pressure is about 12 MN/m^2. Oxidation, or "wet combustion," occurs as air is injected into the system.

Should SO_2 controls become necessary on existing or planned incinerator facilities because of high processing volumes or high sulfur sludges, it is anticipated that stack gas cleaning processes, such as those discussed in Section 3.4, would be effective in reducing SO_2 emissions.

REFERENCES FOR CHAPTER 4

1. K. T. Semrau. "Control of Sulfur Oxide Emissions from Primary Copper, Lead and Zinc Smelters - A Critical Review." Journal of the Air Pollution Control Association, 21(4):185-194, April 1971.

2. T. J. Browder. "Modern Sulfuric Acid Plant Technology." Chemical Engineering Progress, 67(5):45-50, May 1971.

3. Personal Communication - F. L. Porter (EPA) with M. Schmidt (Lurgi), Lurgi Chemie and Huttentechnik GMBH- Frankfort, West Germany, August 29, 1972.

4. Systems Study for Control of Emissions - Primary Nonferrous Smelting Industry. Arthur G. McKee & Co., Western Knapp Engineering Division; Public Health Service, Contract No. PH 86-65-85, June 1969.

5. Engineering and Mining Journal, 173(7):132, July 1972.

6. "Outokumpu Process for the Production of Elemental Sulfur from Pyrites." Sulfur, No. 50, 33-38, 1964.

7. J. C. Fedoruk and W. D. Hunter. "Development and Commercialization of SO_2 Reduction Technology by Allied Chemical Corporation." Paper presented at the European Commission for Economics of the United Nations-Seminar on the Control of Emissions from the Nonferrous Metallurgical Industries, October 1972.

8. Personal communication - F. L. Porter (EPA) with J. J. Nicholson (Cominco), Cominco Ltd., Trail, British Columbia, September 25, 1972.

9. R. B. Thompson and W. W. Jukkola. Pyrites and Sulfide Ore Burners or Roasters, Manufacture of Sulfuric Acid, 61-84. Reinhold Publishing Co., New York, New York, 1959.

10. Personal communication - F. L. Porter (EPA) with L. V. Lee (Dorr-Oliver), Dorr-Oliver, Inc., Stanford, Connecticut, October 2, 1972.

11. Personal communication - F. L. Porter (EPA) with A. Suqanuma (Mitsubishi), Mitsubishi Metal Co., Maoshima, Japan, September 9, 1972.

12. Personal communication - F. L. Porter (EPA) with E. R. Marble, Jr. (Consulting Engineer), Metuchen, N. J., September 26, 1972.

13. F. D. Rovang. Report of visit to Cities Service Smelter, Copperhill, Tennessee, July 19, 1972.

14. R. T. Jacobs. Report of visit to Phelps Dodge Copper Smelter, Ajo, Arizona, February 9, 1972.

15. R. D. Rovang. Report of communication with J. R. Henderson, June 19, 1972.

16. A. L. Kohl and F. C. Riesenfeld. Gas Purification. McGraw Hill, New York, 1970, pp. 202-204.

17. R. A. King. "Economic Utilization of Sulfur Dioxide from Metallurgical Gases." Industrial and Engineering Chemistry, 42, November 1950.

18. L. J. Nicholson. "Cominco's Air Pollution Control Practice." Paper presented at AIChE 66th National Meeting, August 1969.

19. R. T. Jacobs. Report of visit to Cominco Lead and Zinc Smelter in Trail, British Columbia, September 9, 1971.

20. Personal communication - L. T. Nicholson with K. T. Semrau, October 10, 1969.

21. D. F. Carey and N. T. Georgieff. Report of visit to Allied Chemical Corporation, Newell, Pa., July 26, 1972.

22. Estimates of Office of Air Quality Planning and Standards. U. S. Environmental Protection Agency, Research Triangle Park, N. C.

23. Journal Sulfuric Acid and Industry (Japan), September 1971, pp. 16-21.

24. R. W. Dunlap, et al., Environmental Studies Institute, Carnegie-Mellon University, Pittsburgh, Pa., November 1971.

25. J. E. Ludberg. "Removal of Hydrogen Sulfide from Coke Oven Gas by the Stretford Process." Presented at 64th Annual Meeting of Air Pollution Control Association, Atlantic City, N. J., June 27-July 2, 1971.

26. H. W. Elder, et al. Sulfur Oxide Control Technology Visits in Japan. Interagency Technical Committee Report, TVA, Muscle Shoals, Ala., October 1972.

27. Control Systems Laboratory, National Environmental Research Center, Research Triangle Park, N. C.

28. G. N. Thoen, C. C. Dellass, R. G. Tallent, and A. S. Davis. "The Effect of Combustion Variables on the Release of Odorous Sulfur Compounds from a Kraft Recovery Unit." Preprint. (Presented at 1968 annual of TAPPI).

29. Systems Study for Control of Emissions - Primary Nonferrous Smelting Industry. Arthur G. McKee & Co., Western Knapp Engineering Division; Public Health Service, Contract No. PH-86-65-85, June 1969.

30. W. S. Lea and E. A. Cristoferson. "Save Money by Stopping Air Pollution." Chemical Engineering Progress, 61(11):89-93, November 1965.

31. C. I. Harding and S. F. Galeano. "Utilization of Weak Black Liquor for SO_2 Removal and Recovery." Preprint. (Presented at 52nd Annual TAPPI Meeting, New York, February 22, 1967).

32. S. F. Galeano, and C. I. Harding. "Sulfur Dioxide Removal and Recovery from Pulp Mill Power Plants." J. Air Pollution Control Assoc., 17(8): 536-539, August 1967.

33. L. M.NcNay. "Coal Refuse Fires, An Environmental Hazard." Information Circular 8515, Bureau of Mines, Department of the Interior, 1971.

34. R. C. Flegal and J. J. Gahr. "A Summary Report on Demonstration Methods for Extinguishing Culm-Bank Fires." Office of Air Programs, Environmental Protection Agency, November 1971.

35. H. E. Norris. "Scrubbing Sewage Gas." Water Works and Sewerage, 90(2): 61, February 1943.

36. A. M. Buswell. "Gas Scrubbing for H_2S Removal and Methane Enrichment." Public Works, 92(3):112-114, 198, March 1961.

37. "Task Force on Sewage Sludge Incineration." EPA Report, January 1972.

5. SULFUR OXIDE DISPERSION FROM STACKS

5.1 INTRODUCTION

Although stacks are not sulfur oxide emission gas cleaning devices, ground level pollution in the near vicinity of power stations is being reduced in many instances by the use of tall stacks. Compared with the same reduced emission at low levels, a tall stack in open terrain significantly reduces the ground level concentration of small particulates or gases. The reduction results from atmospheric dilution of the effluent before it reaches the ground. Although a tall stack permits maximum atmospheric dilution of contaminants, there is less dilution under some topographical configurations than in others, and contaminants may arrive at ground level in undesirable concentrations. In areas of elevated terrain, for instance, aerodymanic downwash may cause significant ground level concentrations.

In deep narrow valleys and under stable atmospheric conditions, the plume may impact on the valley side. Differences between ground level concentration for tall and short stacks become insignificant as distances from the stack increase; thus, tall stacks are not a substitute for effective emission control.

Pollutant dispersion is affected by the initial rise of the effluent due to its momentum and buoyancy (plume rise) and the downwind spreading from the effective source height (stack height plus plume rise). Stack height, temperature, and velocity of the effluent wind speed and thermal stratification, and topography are important factors influencing ground level concentrations.

References which provide more comprehensive information on sulfur oxide dispersion from stacks are cited in Section 5.2.

5.2 BIBLIOGRAPHY

5.2.1 Guides, Manuals, Workbooks

1. Munn, R. E., "Annotated Bibliography for Air Pollution Meteorolgv", J. Air Pollution Control Accosc., Vol. 11(10), pp. 449-453, 1968.
2. "Recommended Guide for the Prediction of Dispersion of Airborne Effluents", American Society of Mechanical Engineers, United Engineering Center, New York, 1968.
3. Slade, E. 9ed.) "Meteorology and Atomic Energy, 1968", U. S. Atomic Energy Commission, Div. of Technical Information, Oak Ridge, Tenn., 1968.
4. "Tall Stacks, Various Atmospheric Phenomena and Related Aspects, as Annotated Bibliography", National Air Pollution Control Administration, Office of Technical Information and Publications, Air Pollution Technical Information Center, Arlington, Virginia, August 1968.
5. Turner, D. B., "Workbook of Atmospheric Dispersion Estimates", U. S. Dept. of Health, Education and Welfare, National Air Pollution Control Administration, PHS-Pub-999-AP 26, 1967, pp. 31-34.

5.2.2 Textbooks

1. Junge, C. E., "Air Chemistry and Radioactivity", Academic Press, New York, 1963.
2. Lumley, J. L. and Panofsky, H. A., "The Structure of Atmospheric Turbulence", John Wiley & Sons, Inc., New York, pp. 3, 1964.
3. McGill, P. L., Holden, F. R., and Ackley, C. (eds.), "Air Pollution Handbook", McGraw-Hill, New York, 1956.
4. Munn, R. E., "Descriptive Micrometeorology", Academic Press, New York, 241 pp., 1966.
5. Pasquill, F., "Atmospheric Diffusion", D. Van Nostrand, New York, 297 pp, 1962.
6. Schlichting, H., "Boundary Layer Theory", McGraw-Hill, New York, 1960.
7. Scorer, R. S., "Air Pollution", Pergamon, London, 151 pp., 1968.
8. Scorer, R. S., "Natural Aerodynamics", Pergamon, New York, 1958.
9. Sporn, P., and Smith, M., "Report to the Prime Minister on the Sitting of Power Station for Adding 428,000 KW to the Power System of the Israel Electric Corporation", (Hebrew Edition), March, 1968.
10. Stern, A. C., (ed.) "Air Pollution, Vol. 1, Air Pollution and Its Effects", Academic Press, New York, 694 pp., 1968.
11. Stern, A. C., (ed.) "Air Pollution Handbook", Academic Press, New York, 1968.

12. Sutton, O. G., "Micrometeorology", McGraw-Hill, New York, 333 pp., 1953.

5.2.3 General

1. Beers, N. R., "Stack Meteorology and Atmospheric Disposal of Radioactive Waste", Nucleonics, Vol. 4, pp. 28-38, 1949.

2. Bierly, E. W. and Hewson, E. W., "Some Restrictive Meteorological Conditions in the Design of Stacks", J. Applied Meteorol., Vol 1(13): 383-390, Sept., 1962.

3. Brink, J. A., Jr., and Crocker, B. B., "Practical Applications of Stacks to Minimize Air Pollution Problems", 57th National Meeting of the Air Pollution Control Assoc., Houston, Texas, June, 1965.

4. Clarke, A. J., Lucas, D. H., and Ross, F. F., "Tall Stacks--How Effective are They?", Clean Air, Vol. 1(1): 18-29, 1971.

5. Davidson, W. F., "The Dispersion and Spreading of Gases and Dust from Chimneys", Transactions of the Conference on Industrial Wastes, 14th Annual Meeting, Industrial Hygiene Foundation of America, pp. 38-55, 1949.

6. "Full-Scale Study of Inversion Breakup at Large Power Plants", Tennessee Valley Authority, Division of Enviromnemtal Research and Development Report, 1970.

7. Gartrell, E. E., et al., "Full-Scale Study of Dispersion of Stack Gases, a Summary Report", Tennessee Valley Authority and Public Health Service, Chattanooga, Tennessee, 93 pp, 1964.

8. Gartell, F. E., Thomas, F. W., and Leavit, J. M., "Dispersion Characteristics of Stack Emissions from Large Thermal Power Station", (Presented at Joint Meeting of American Meteorology Society and American Geophysical Union, Washington, D. C., April 19-22, 1966.)

9. Hewson, E. W. and Gill, G. C., "Meteorological Investigations in Columbia River Valley Near Trail, British Columbia", In: Report Submitted to the Trail Smelter Arbitral Tribunal, U. S. Bureau of Mines, Bulletin 453, pp. 23-228, 1944.

10. Johnson, Warren B., Jr. and Uthe, Edward E., "LIDAR Study of Stack Plumes", Final Report, National Air Pollution Control Administration Contract PH 22-68-33, 1970.

11. Power Plant Effluent Study, Volume 1, Instrumentation Procedures and Data Tabulations, 1968", National Air Pollution Administration, U. S. Department of Health, Education and Welfare, NAPCA Pub. No. APTD 70-2, 1970.

12. Lowry, P. H., "Microclimate Factors in Smoke Pollution from Tall Stacks", Meteorological Monographs, Vol. 6(4): 24-29, 1951.

13. Montgomery, T. L., Carpenter, S. B., and Lindley, H. E., "The Relationship Between Peak and Mean SO_2 Concentrations", Conference on Air Pollution Meteorology, Raleigh, N. C., April 1971.

14. Nieman, Brand L., Day, Margaret C., and MacCready, Paul B., Jr., "Particulate Emissions, Plume Rise, and Diffusion from a Tall Stack", Vol. 1, Technical Report, National Air Pollution Control Administration Contract CPA 22-69-20, 1970.

15. Rummerfield, P. S., Cholak, J., and Kereiakes, J., "Estimation of Local Diffusion of Pollutants from a Chimeny: A Prototype Study of Employing an Activated Tracer", American Industrial Hygienic Assoc. J., pp. 366-371, August 1967.

16. Smith, M. E., "Reduction of Ambient Air Concentrations of Pollutants by Dispersion from High Stacks", U. S. Dept. of Health, Education and Welfare, Public Health Service, PHS-Pub. 1649, pp. 151-160. (Proceedings: Third National Conference on Air Pollution, Washington, D. C., December 12-14, 1966).

17. Sporn, P. and Frankenberg, T. T., "Pioneering Experiments with High Stacks on the Ohio Valley Electricity Corporation and the American Power Systems", In: Proceedings: International Clean Air Congress, London, October 1966. (Expanded Version of this paper appears in "The Tall Stack", a collection of papers by Philip Sporn, Retired President, American Electric Power Company, New York, 1967.

18. Stone, G. N. and Clarke, A. J., "British Experience and Tall Stacks for Air Pollution Control on Large Fossil-Fueled Power Plants", American Power Conference, Illinois Institute of Technology, April 27, 1967.

19. "Tall Stacks, Various Atmospheric Phenomena and Related Aspects", National Air Pollution Control Administration, U. S. Department of Health, Education and Welfare, NAPCA Pub. No. APTI) 70-2, 1970.

5.2.4 Plume Rise, Stack Height

1. Bordurtha, F. T., Jr., "The Behavior of Dense Stack Gases", J. Air Pollution Control Assoc., Vol. 11(9), 431, 1961.

2. Bosanquet, C. H., "The Rise of a Hot Waste Gas Plume", J. Inst. Fuel., Vol. 30 (197): 322-328, 1957.

3. Briggs, G. A., "A Plume Rise Model Compared with Observations", J. Air Pollution Control Assoc., Vol. 15(9): 433-438, 1965.

4. Briggs, G. A., "Plume Rise", U. S. Atomic Energy Commission Report TIS-25075, pp. 1-81, 1969.

5. Briggs, G. A., "A Simple Model for Bent-Over Plume Rise", Doctoral Dissertation, The Pennsylvania State University, December 1970.

6. Briggs, G. A., "Some Recent Analyses of Plume Rise Observations", Paper Presented at 1970 International Air Pollution Conference of the International Union of Air Pollution Presentation Association.

7. Bringfelt, B., "Plume Rise Measurements at Industrial Chimneys", Atmos. Environ., Vol. 3, 575-598, 1968.

8. Bringfelt, B., "A Study of Buoyant Chimney Plumes in Neutral and Stable Atmospheres", Atmos. Environ. 3, 609, 1969.

9. Bryant, L. W. and Cowdrey, C. F., "The Effects of the Velocity and Temperature of Discharge on the Shape of Smoke Plumes from a Funnel or Chimney: Experiments in a Wind Tunnel", Proceedings, Institute of Mechanical Engineers (London), Vol. 169, pp. 371-400, 1955.

10. "The Calculation of Atmospheric Dispersion from a Stack, Report of CONCAWE Working Group on Stack Height and Atmospheric Dispersion", CONCAWE, Hague, The Netherlands, 57 pp, 1966.

11. Carpenter, S. B., Frizcha, J. A., Smith, M. W., Leavitt, J. M. and Thomas, F., "Report on a Field Scale Study of Plume Rise at Large Electric Generating Stations", Paper 67-82, 60th Annual Meeting of the Air Pollution Control Association, Cleveland, Ohio, 1967.

12. Carpenter, S. B., Thomas, F. W., and Gartrell, F. E., "Full-Scale Study of Plume Rise at Large Electric Generating Station", Tennessee Valley Authority, Muscle Shoals, Alabama, September 1968.

13. Carpenter, S. B., et al., "Principal Plume Dispersion Models, TVA Power Plants", Presented APCA, St. Louis, June 1970.

14. Carson, J. E. and Moses, H., "Validity of Currently Popular Plume Rise Formulas", USAEC Meteorological Information Meeting, September 11-14, 1967, Chalk River, Canada, AECL-2787, pp, 1-15.

15. Fan, L., "Turbulent Buoyant Jets into Stratified or Flowing Ambient Fluids", California Institute of Technology, Report KH-R-15, 1967.

16. Fay, J. A., Escudier, M. and Hoult, D. P., "A Correlation of Field Observations of Plume Rise", MIT Fluid Mech. Lab. Report, 1969, pp. 1-29.

17. Fischer, R. D., Flanigan, L. J., and Putnam, A. A., "Prediction of the Rise of a Gaseous Plume in a Calm Atmosphere with any Lapse-Rate Profile", Proc. 2nd Int. Clean Air Congress, 1007-1018, 1971.

18. Gifford, F. A., "The Rise of Strongly Radioactive Plumes", J. Appl. Meteor., 6, 644-649, 1967.

19. Hamilton, P. H., "Plume Height Measurements at Two Power Stations", Atmos. Environ., Vol 1, 379, 1967.

20. Hoult, D. P., Fay, J. A. and Forney, L. J., "A Theory of Plume Rise Compared with Field Observations", Paper 68-77, Delivered at 61st Annual Meeting of the Air Pollution Control Association, pp. 1-19, 1968.

21. Landers, W. S., "Trends in Steam Station Design Affecting Air Pollution", American Society of Mechanical Engineers, Un. Engineering Center, New York, 66-PWR-1, 1966.

22. Lucas, D. H., "Comment during Symposium on the Dispersion of Cnimney Gases Held on December 7, 1961, Royal Meteorological Society", Int. J. Air Water Pollution, Vol. 6, p. 94, 1962.

23. Morton, B. R., "The Ascent of Turbulent Forced Plumes in a Calm Atmosphere", Intern. J. Air Poll., Vol. 1, 184, 1959.

24. Morton, B. R., "Forced Plumes, J. Fluid Mech. Vol. 5 (1), 151, 1959.

25. Moses, H. and Carson, J. W., "Stack Design Parameters Influencing Plume Rise", Paper 67-84, 60th Annual Meeting of the Air Pollution Control Association, Cleveland, Ohio, 1967.

27. "Round Table on Plume Rise and Atmospheric Dispersion. Atmospheric Environment", Pergamon Press, New York, Vol. 2, 1968.

5.2.5 Downwind Dispersion

1. Barad, M. L., "Diffusion of Stack Gases in Very Stable Atmosphere", Meterological Monographs", Vol. 1(4): 9-19, 1958.

2. Bodurtha, F. T., "Diffusion of ASME Standard APS-1", Un. Engineering Center, New York.

3. Bodurtha, F. T., "Background and Basis of ASME Standard, Recommended Guide for the Control of Dust Emission--Combustion for Indirect Heat Exchanger", American Society of Mechanical Engineers, Un. Engineering Center, New York, APS-1

4. Bosanquet, C. H.,,Carey, W. F. and Halton, E. M., "Dust from Chimney Stacks", Proceedings of the Institute of Mechanical Engineers, Vol. 1 162, pp. 355-367, 1950

5. Bosanquet, C. H. and Pearson, J. L., "The Spread of Smoke and Gases from Chimneys, Disperse Systems in Gases", Trans. Faraday Soc., Vol. 32, pp. 1249-1264, 1936.

6. Bowne, N. E., "Some Measurements of Diffusion Parameters from Smoke Plumes", Bulletin of the American Meteorological Society, Vol. 42(2): 101, 1961.

7. Brummage, K. G., "The Calculation of Atmospheric Dispersion from a Stack", Atmos. Env., 2, 197-224, 1968.

8. Bryant, P. M., "Effect of Diluting Stack Gases on Downwind Concentration", Nucl. Safety, Vol. 8(2): 161 (Winter 1966-67).

9. Calder, K. L., "Some Recent British Work on the Problem of Diffusion in the Lower Atmosphere", In: Air Pollution, Proceedings of the U. S. Technical Conference on Air Pollution, McGraw-Hill, New York, 1952, pp. 787-792.

10. "The Cardinal Plant Story", American Electric Power Engineering Staff, Elec. World, Vol. 167(12): 89, March 20, 1967.

11. Chaudhry, F. H. and Meroney, R. N., "Turbulent Diffusion in a Stably Strafified Shear Layer", Task II B Research Technical Report Desert Test Center, TR ECOM-0423-5, (Fluid Dynamics and Diffusion Laboratory Report CER69-70FHC-NM12), Colorado State University, September 1969.

12. Cramer, H. E., "A Practical Method for Estimating the Dispersal of Atmospheric Contaminants", Proc., First Nat'l. Conf. on Appl. Meterol. Amer. Meteorol. Soc., C., Hartford, Conn., pp. 33-35, October 1957.

13. Gifford, F. A., "Use of Routine Meteorological Observations for Estimating Atmospheric Dispersion", Nuclear Safety, Vol. 2(4): 47-51, 1961.

14. Gifford, F. A., "Peak to Average Concentration Ratios According to a Fluctuating Plume Dispersion Model", International J. of Air Pollution, 3(4): 253-260, 1960.

15. Halitsky, J., Golden, J., Halpern, P. and Wu, P., "Wind Tunnel Tests of Gas Diffusion from a Peak in the Shell of a Nuclear Power Reactor and from a Nearby Stack", Geophysical Sciences Laboratory Report No. 63-2, New York University, April 1963.

16. Hilst, G. R., "The Dispersion of Stack Gases in Stable Atmospheres", J. Air Pollution Control Assoc., 7(3), 205-210, 1957.

17. Hilst, G. R. and Simpson, C. L., "Observations of Vertical Diffusion Rates in Stable Atmospheres", J. Meteorol., Vol. 15(1): 125-126, 1957.

18. Lowry, P. H., Mazzarella, D. A. and Smith, M. E., "Ground-Level Measurements of Oil-Fog Emitted from a Hundred-Meter Chimney", Meteorological Monographs, Vol. 1(4): 30-35, 1951.

19. Lucas, D. H., "Application and Evaluation of Results of the Tilbury Plume Rise and Dispersion Experiment", Atmos. Env., Vol. 1: 421-424, 1967.

20. McLaughlin, J. F., Smith, M. E. and Singer, I. A., "Survey of Ground-Level SO_2 Concentrations Near Alton, Illinois", Proc., 2nd Int. Clean Air Congress, 1056-1061, 1971.

21. Moore, D. J., "Concentration Measurements Near Tilbury Power Station", Atmos. Env., 1: 389-410, 1967.

22. Pasquill, F., "The Estimation of Dispersion of Wind-borne Materials". Meteorol. Mag., Vol. 90, pp. 33-49, 1961.

23. Pasquill, F. and Smith, F. B., "The Physical and Meteorological Basis for the Estimation of the Estimation of the Dispersion of Windborne Material", Proc., 2nd Int. Clean Air Congress, 1067-1072, 1971.

24. Peterson, K. R., "Continuous Point Source Plume Behavior Out to 160 Miles", J. Applied. Meteorol., Vol. 7, pp. 217-226, April 1968.

25. Pooler, F. and Niemeyer, L. E., Dispersion from Tall Stacks" An Evaluation", Proc., 2nd Int. Clean Air Congress, 1049-1056, 1971.

26. Pooler, F., "Potential Dispersion of Plumes from large Power Plants", PHS-Pub-000-AP-16, 13 pp.

27. Priestly, C. H., McCormick, R. A., and Pasquill, F., "Turbulent Diffusion in the Atmosphere", World Meteorological Organization, Geneva, Switzerland, Technical Note 24, WMO 77, TP 31, 1958.

28. Schmidt, F. H., "On the Rise of Hot Plumes in the Atmosphere", Int. J. Air Water Poll., Vol. 9, 175, 1965.

29. Scriven, R. A., "Properties of the Maximum Ground Level Concentration from an Elevated Source", Atmos. Env., Vol. 1, 411-419, 1967.

30. Smith, M. E. and Singer, I. A., "An Improved Method of Estimating Concentrations and Related Phenomena from a Point Source Emission", J. Applied Meteorol., Vol. 5, pph. 631-639, October 1966.

31. Ukeguchi et al., "Study on Stack Gas Diffusion", Mitsubishi Technical Bulletin No. 52, Japan, August 1967.

5.2.6 Mathematical Diffusion Models

1. Clarke, J. F., "A Simple Diffusion Model for Calculating Point Concentrations from Multiple Sources", J. Air Pollution Control Assoc., Vol. 4 (9): 347-352, September 1964.

2. Davidson, B., "Summary of the New York Urban Air Pollution Dynamics Research Program", J. Air Pollution Control Assoc., Vol. 17(3): 154-158, March 1967.

3. Fan, L. T. and Horie, Y., "Review of Atmospheric Dispersion and Urban Air Pollution Models", CRC, Critical Reviews in Environmental Control, 431-457, 1971.

4. Koogler, J. B., Sholtes, R. S., Danis, L. and Harding, C. I., "A Multivariant Model for Atmospheric Dispersion Predictions", J. Air Pollution Control Assoc., Vol. 17 (4): 211-214, April 1967.

5. Leavitt, J. M., "Meteorological Considerations in Air Quality Planning", J. Air Pollution Control Assoc., Vol. 10, pp. 246-250, June 1960.

6. Lyons, Walter A. and Cole, H. S., "Fumigation and Plume Trapping: Aspects of Mesoscale Dispersion on the Shores of Lake Michigan in Summer During Periods of Stable Onshore Flow", 42-47, Conference on Air Pollution Meteorology, Raleigh, N. C., 1971.

7. Martin, D. O. and Tikvart, J. A., "A General Atmospheric Diffusion Model for Estimating and Effects of One or More Sources on Air Quality", (Presented at Annual Meeting of Air Pollution Control Assoc., St. Paul, Minnesota, June 1968).

8. Miller, M. E. and Holzworth, G. C., "An Atmospheric Diffusion Model for Metropolitan Area", J. Air Pollution Control Assoc., Vol. 17(1): 46-50, January 1957.

9. Pooler, F., Jr., "A Predication Model of Mean Urban Pollution for Use with Standard Wind Roses", Int. J. Air and Water Pollution, Vol. 4(3/4): 199=211, September 1961.

10. Szepesi, D. J., "A Model for the Long Term Distribution of Pollutants Around a Single Source", Idojaras (Budapest), Vol. 68, pp. 257-269, Sept.-Oct. 1964.

11. Turner, D. B., "Relationship Between 24-Hour Mean Air Quality Measurements and Meteorological Factors in Nashville, Tennessee", J. Air Pollution Control Assoc., Vol. 11(10): 483-489, 1961.

12. Turner, D. B., "A Diffusion Model for an Urban Area", J. Applied. Meteorol., Vol. 3(1): 83-91, February 1964.

5.2.7 Aerodynamics, Wind Tunnel Studies

1. Coonihan, J., "An Improved Method of Simulating an Atmospheric Boundary Layer in a Wind Tunnel", Atmos. Environ., Vol. 3, 197, 1969.

2. Culkowski, W. M., "Estimating the Effect of Buildings on Plumes from Short Stacks", Nucl. Safety, Vol. 8(3), 247 (Spring 1967).

3. Halitsky, J., "Diffusion of Vented Gas Around Buildings", J. Air Pollution Control Assoc., 12(2): 74-80, 1962.

4. Halitsky, J., "Gas Diffusion Near Buildings, Theoretical Concepts and Wind Tunnel Model Experiments with Prismatic Building Shapes", New York University, Geophysical Sciences Lab., Report 63-3, 1963.

5. Inoue, E., "On the Structure of Wind Near the Ground", Bull. Natl. Inst. Agr. Sci. (Japan), Series A, No. 2, September 1952.

6. Martin, J. E., "The Correlation of Wind Tunnel and Field Measurements of Gas Diffusion Using Kr-85 as a Tracer", Ph.D Thesis, MMPP 272, University of Michigan, June 1965.

7. Meroney, R. W., et al., "Simulation of Atmospheric Motion by Wind-Tunnel Flows", Colorado State University, Report Number CER66-JEC-VAS-EJP-GJB-HC-RNM-SI-17, May 1966.

8. "Report of Government Committee on Air Pollution", Sir Hugh Beaver (Chairman), Her Majesty's Stationery Office, London, Cmd. 9322, 1954.

9. Scorer, R. S., "The Behavior of Plumes", Int. J. Air Pollution, Vol. 1, pp. 198-220, 1959.

10. Sherlock, R. H. and Lesher, E. J., "Design of Chimneys to Control Downwash of Gases", Trans. Am. Soc. Mech. Engrs., Vol. 77, pp. 1-9.

11. Sherlock, R. H. and Lesher, E. J., "Role of Chimney Design in Dispersion of Waste Gases", Air Repair, Vol. 4(2), 1-10, 1954.

12. Strom, G. H., "Wind Tunnel Scale Model Studies of Air Pollution from Industrial Plants", Industrial Wastes, Sept.-Oct., Nov.-Dec., 1955, Jan.-Feb. 1956.

13. Strom, G. H., Hackman, M. and Kaplin, E. J., "Atmospheric Dispersion Industrial Stack Gases Determined by Concentration Measurements in Scale Model Wind Tunnel Experiments", J. Air Pollution Control Assoc., Vol. 7(3): 198-203, 1957.

14. Sutton, O. G., "Discussion Before Institute of Fuels", J. Institute of Fuel, Vol. 33, pp. 495, May 1960.

5.2.8 Natural Removal Processes

1. Brohult, Sven, "The Sulfur Problem and Air Pollution", Annual Report to the National Academy of Engineers", Sweden, 1967.

2. Chamberlain, A. C., "Aspects of Travel and Deposition of Aerosol and Vapour Clouds", Atomic Energy Research Establishment, Harwell, England, HP/R, 1261, 35 pp. 35, 1955.

3. Coleman, R., "The Importance of Sulfur as a Plant Nutrient in World Crop Production", Soil Science, Vol. 101(4): 230-238, 1966.

4. Culkowski, W. M. "Calculations of the Deposition of Aerosols from Elevated Sources", Oak Ridge Operations Office (AEC), Report ORO-171, 1958.

5. Culkowski, W. M., "Deposition and Washout Computations Based on the Generalized Gaussian Plume Model:, U. S. Weather Bureau, Oak Ridge, Tennessee, USAEC Report ORO-599, 1963.

6. Englemann, R. J., Perkins, R. W., Hage, D. I. and Haller, W. A., "Wash Coefficients for Selected Gases and Particulates", Preprint, (Presented at the 59th Annual Meeting of the Air Pollution Control Assoc., San Francisco, Calif., June 20-24, 1966.

7. Eschenroeder, Alan, and Martinez, Jose R., "An Extension of K-Theory to Describe Photochemical Air Pollution", Conf. on Air Pollution Meteorology, 69-74, April 1971.

8. Gartrell, F. E., Thomas, F. W. and Carpenter, S. B., "Atmospheric Oxidation of SO_2 in Coal-Burning Power Plant Plumes", A,er/ Omd. Hyg. Assoc. J., Vol. 24, pp. 113-120, March-April, 1963.

9. Gifford, F. A. and Pack, D. H., "Surface Deposition of Airborne Material", Nuclear Safety, Vol. 3(4): 76-80, 1962.

10. Hales, J. M., Thorp, J. M. and Wolf, M. A., "Theory and Field Measurements of Sulfur Dioxide Washout from an Elevated Plume", Conf. on Air Pollution Meteorology, Raleigh, N. C., 63-64, April 1971.

11. Hanst, Philip L. and Bufalini, Joseph J., "Nitrogen-Oxygen Compounds in Atmospheric Photochemistry", Conf. on Air Pollution Meteorology, Raleigh, N. C., 75-79, April 1971.

12. Junge, C. E., "Air Chemistry and Radioactivity", Academic Press, New York, 1963.

13. Lodge, James P., Jr., "Transformation and Removal of Atmospheric Pollutants", Conf. on Air Pollution Meteorology, Raleigh, N. C., 62, April 1971.

14. Semonin, Richard G. and Adam, John R., "The Washout of Atmospheric Particulates by Rain", Conf. on Air Pollution Meteorology, Raleigh, N. C. 65-68, April 1971.

15. Singer, I. A. and Smith, M. E., "The Influence of Variable Meteorological Parameters on Diffusion Deposition and Washout from Point Sources", Preprint (Presented at the 58th Annual Conference, Air Pollution Control Assoc., Toronto, Canada, June 1965).

5.2.9 Topographic and Urban Effects

1. DeMarrais, G. A., "Vertical Temperature Difference Observed Over an Urban Area", Bulletin American Meteorological Society, Vol. 42, pp. 548-556, 1961.

2. Landsberg, H., "Physical Climatology", Gray, DuBois, Penn., p. 326, 1966.

3. Neiburger, M., "The Dispersion and Deposition of Air Pollutants Over Cities Symposium", Air Over Cities, Public Health Service, Cincinnati, Ohio, SEC Technical Report A62-5, pp. 156-157, 1961.

4. "Symposium: Air Over Cities", U. S. Public Health Service, R. A. Taft Sanitary Engineering Center", Cincinnati, Ohio, SEC Technical Report A62-5, 290 pp., 1961.

5. Smith, T. B., "Diffusion Study in Complex Mountainous Terrain", Meteorology Research, Inc., Report to Dugway Proving Ground Army Chemical Corps., AD484087, pp. 106-110, 1965.

6. Van der Hoven, I., "Atmospheric Transport and Diffusion at Coastal Sites", Nuclear Safety, Vol. 8(5): 490-499, 1967.

5.2.10 Air Pollution Climatology

1. Department of Health, Education and Welfare, "Air Pollution Prevention and Control, Definition of Atmospheric Areas", Federal Register, Vol 33(10), January 1968.

2. Hosler, C. R., "Low-Level Inversion Frequency in the Contiguous United States", Monthly Weather Review, Vol. 89, pp. 319-339, September 1961.

3. Holzworth, G. C., "Estimates of Mean Maximum Mixing Depths in the Contiguous United States", Monthly Weather Review, Vol. 92, pp. 235-242, 1964.

4. Holzworth, G. C., "Mixing Depths-Wind Speed and Air Pollution Potential for Selected Locations in the United States", J. Appl. Meteor., 6, 1039-1044, 1967.

5. Korshover, J., "Climatology of Stagnating Anticyclones East of the Rocky Mountains, 1936-1965", PHS-Pub-999-AP-34, 15 pp, 1967.

5.2.11 Costs

1. Nelson, F. and Shenfeld, L., "Economics, Engineering and Air Pollution in the Design of Large Chimneys", J. Air Pollution Control Assoc., Vol. 15(8): 355-361, August 1965.

5.2.12 Aviation Regulations

1. "Federal Aviation Regulations, Part 77", Dept. of Transporation Federal Aviation Administration, Washington, D. C.

6. EMISSION FACTORS

It is often necessary to estimate emissions from sources for which accurate stack gas analyses are unavailable. In some cases, the proper use of a good emission factor will yield better results than those based on a single series of stack gas tests. Emission factors are based on past stack gas sampling data, material balances, and engineering estimates for sources that are similar to those in question.

Table 6-1 is a compilation of available emission factors for sulfur compounds from various types of sources. Most of the sulfur emitted is in the form of SO_2, but smaller quantities of SO_3, sulfuric acid mist (usually reported as particulate matter), hydrogen sulfide, and various other forms of sulfur are also emitted. The emission factors listed are for uncontrolled sources and are reported as SO_2 unless otherwise noted. For a specific source where control equipment is used, the listed uncontrolled emission rates must be multiplied by 1.0 minus the fractional efficiency of the control equipment. Unless otherwise stated, these factors are based on Reference 1. For further details on the range of emissions and conditions which affect these factors, the reader should refer to this reference work.

Table 6-1. EMISSION FACTORS FOR SULFUR OXIDES[1]

Type of Emission Source	Emission rate (g/kg)[a]
STATIONARY FUEL COMBUSTION SOURCE	
Bituminous Coal:	
Furnace greater than 30 MJ/s	19S[b]
General	19S[b]
Wet bottom	19S[b]
Dry bottom	19S[b]
Cyclone	19S[b]
Furnace from 3 to 30 MJ/s	19S[b]
Hand-fired unit	19S[b]
Anthracite Coal:	
Dry bottom	19S
Overfeed stoker	19S
Hand-fired unit	18S
Fuel Oil:	
Power plant	kg/m^3 19S
Industrial/commercial unit	
Residual	kg/m^3 19S
Distillate	kg/m^3 17S
Domestic	kg/m^3 17S
Natural Gas:	
Power plant	kg/hm^3 9.6
Industrial process boiler	kg/hm^3 9.6
Domestic/commercial heating unit	kg/hm^3 9.6
Liquified Petroleum Gas (LPG)	
Industrial process furnace	
Butane	kg/m^3 0.005 S
Propane	kg/m^3 0.005 S
Domestic/commercial furnace	
Butane	kg/m^3 0.005 S
Propane	kg/m^3 0.005 S
Wood and Bark	0 - 1.5

See footnotes at the end of the table.

EMISSION FACTORS FOR SULFUR OXIDES--Continued

Type of Emission Source	Emission rate (g/kg)[a]
SOLID WASTE DISPOSAL	
Refuse Incinerator:	
Municipal multiple chamber	
Without settling chamber and water spray system	0.75
With settling chamber and water spray system	0.75
Industrial/commercial	
Multiple chamber	0.75
Single chamber	0.75
Controlled air	0.75
Flue-fed	0.25
Modified flue-fed	0.25
Domestic single chamber	
Without primary burner	0.25
With primary burner	0.25
Pathological	Neg
Conical Burner:	
Municipal refuse	1.0
Wood (depending on burner adjustment)	0.05
Open Burning:	
Municipal refuse	0.5
Automobile components	Neg
Horticultural refuse	
Agricultural field burning	Neg
Landscape refuse and pruning	Neg
Wood	Neg
MOBILE COMBUSTION SOURCE	
Gasoline-Powered Motor Vehicle	kg/m^3 1.02
Diesel:	
Truck or bus	kg/m^3 3.2
Locomotive	kg/m^3 7.8

See footnotes at the end of the table.

EMISSION FACTORS FOR SULFUR OXIDES--Continued

Type of Emission Source		Emission rate (g/kg)[a]
Aircraft:		
Turbofan		
Jumbo jet	kg/engine-LTO	.91
Long range	kg/engine-LTO	.91
Medium range	kg/engine-LTO	.91
Turbojet	kg/engine-LTO	.91
Turboprop	kg/engine-LTO	.45
Turboshaft	kg/engine-LTO	.45
Piston		
Transport	kg/engine-LTO	.06
Light	kg/engine-LTO	.005
Vessel:		
Steamship		
Underway	kg/km	1.74S[b]
In-berth	kg/day	138 S
Motor ship		
Underway	kg/km	0.37
In-berth	kg/day	19.5
CHEMICAL PROCESS INDUSTRY		
Explosives Manufacture:		
Sulfuric acid regenerator		9.0
Red water incinerator		6.5
Sulfuric acid concentrator		32.5
Sulfuric Acid Production:		
93% conversion of SO_2 to SO_3	g/kg 100% H_2SO_4	48.5
94% conversion of SO_2 to SO_3	g/kg 100% H_2SO_4	42.0
95% conversion of SO_2 to SO_3	g/kg 100% H_2SO_4	35.0
96% conversion of SO_2 to SO_3	g/kg 100% H_2SO_4	27.5
97% conversion of SO_2 to SO_3	g/kg 100% H_2SO_4	20.0
98% conversion of SO_2 to SO_3	g/kg 100% H_2SO_4	13.0
99% conversion of SO_2 to SO_3	g/kg 100% H_2SO_4	7.5
99.5% conversion of SO_2 to SO_3	g/kg 100% H_2SO_4	3.5
METALLURGICAL INDUSTRY		
Coke Manufacture:		
Charging		0.01
Underfiring		5.0

See footnotes at the end of the table.

EMISSION FACTORS FOR SULFUR OXIDES--Continued

Type of Emission Source		Emission rate (g/kg)[a]
Primary Copper Smelting:		
Roasting		30.0
Smelting		160
Converting		435
Primary Lead Smelting:		
Sintering and crushing		330
Blast furnace		330
Reverberatory furnace		330
Primary Zinc Smelting (Roasting)		550
Secondary Lead Smelting:		
Reverberatory furnace		42.5
Blast (cupola) furnace		
Without control		45.0
With NaOH scrubber		0.4
With water spray chamber		23.0
MINERAL PRODUCTS INDUSTRY		
Calcium Carbide Plant:		
Electric furnace main stack		1.5
Coke dryer		1.5
Mineral Wool Processing:		
Cupola		0.01
Reverberatory furnace		Neg
Blow chamber		Neg
Curing oven		Neg
Cooler		Neg
PETROLEUM INDUSTRY		
Petroleum Refinery:		
Boiler and process heater		
Oil-fired	g/m^3	NA[c]
Gas-fired	g/m^3	NA[c]
Fluid catalytic cracker (fresh feed)	g/m^3	1498
Moving-bed catalytic cracker (fresh feed)	g/m^3	171

See footnotes at the end of the table.

EMISSION FACTORS FOR SULFUR OXIDES--Continued

Type of Emission Source	Emission rate (g/kg)[a]
WOOD PROCESSING	
Sulfate pulping recovery boilers and direct-contact evaporators	
Without control	2.5
With electrostatic precipitator	2.5
With venturi scrubber	2.5

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[a] Units other than g/kg are given at the end of the entries immediately preceding numerical values for uncontrolled rates; when controlled rates are known, they are listed by type of control applied.

[b] The letter S on all coal- and oil-fired units indicates that the weight percentage of sulfur in the coal should be multiplied by the value given. For LPG gas-fired units, S is the sulfur content expressed in g/100m^3 of fuel.

[c] Information not available.

REFERENCE FOR CHAPTER 6

1. Compilation of Air Pollutant Emission Factors, EPA Office of Air Programs. Publication AP-42, February 1972.

*U.S. GOVERNMENT PRINTING OFFICE: 1973 546-311/95 1-3